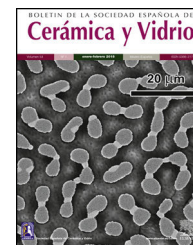




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Original

Basic microstructural, mechanical, electrical and optical characterisation of BaTiAl₆O₁₂ ceramics

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ABSTRACT

In progressive particle or layered composites based on a combination of BaTiO₃ and Al₂O₃, serving as e.g. ceramic harvesters, new phases are formed during heat treatment. The dominant one is BaTiAl₆O₁₂. This study provides information about the microstructural, mechanical and optical properties of the BaTiAl₆O₁₂ ceramics. The evolution of the phases during the solid-state reaction synthesis of the BaTiAl₆O₁₂ was monitored. The fully dense samples prepared by spark plasma sintering had indentation Vickers hardness and indentation elastic modulus within ranges of 10.1–13.7 GPa and 132.0–187.0 GPa, depending on loading force. The three-point bending tests of the BaTiAl₆O₁₂ samples resulted in flexural strength of 129.9 MPa and fracture toughness of 1.8 MPa m^{1/2}. The sample showed blue broad-band emission under UV excitation due to the charge-transfer transition of the Ti⁴⁺ and defect sites. The BaTiAl₆O₁₂ evinced low permittivity (ϵ') = 16 and dielectric loss ($\tan \delta$) < 0.0003 at a frequency 1 kHz.

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Caracterización microestructural, mecánica, eléctrica y óptica básica de cerámicas BaTiAl₆O₁₂

RESUMEN

En los compuestos de partículas o capas progresivas basados en una combinación de BaTiO₃ y Al₂O₃, que sirven, por ejemplo, como capacitadores cerámicos, se forman fases nuevas durante el tratamiento térmico. La dominante es BaTiAl₆O₁₂. Este estudio proporciona información sobre las propiedades microestructurales, mecánicas y ópticas del cerámico BaTiAl₆O₁₂. Se monitorizó la evolución de las fases durante la síntesis por reacción en estado sólido de BaTiAl₆O₁₂. Las muestras totalmente densas preparadas mediante

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spark plasma sintering exhibieron una dureza Vickers por indentación y un módulo elástico por indentación entre 10,1-13,7 GPa y 132,0-187,0 GPa, respectivamente, dependiendo de la fuerza de carga aplicada. Los ensayos de flexión en tres puntos de las muestras de BaTiAl₆O₁₂ dieron como resultado una resistencia a la flexión de 129,9 MPa y una tenacidad a la fractura de 1,8 MPa m^{1/2}. La muestra presentó una emisión azul de banda ancha bajo excitación UV debido a la transición de transferencia de carga del Ti⁴⁺ y sitios defectuosos. El BaTiAl₆O₁₂ mostró una baja permitividad (ϵ') = 16 y una pérdida dieléctrica ($\tan \delta$) < 0,0003 a una frecuencia de 1 kHz.

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Introduction

Barium titanate (BaTiO₃) is one of the most important lead-free polycrystalline ceramic materials with attractive dielectric, ferroelectric and piezoelectric properties. It has found various applications in semiconductors, ultrasonic transducers, piezoelectric devices, pyroelectric detectors, etc. [1,2]. However, barium titanate shows relatively low mechanical characteristics compared with other ceramics. Therefore, the scientific efforts concentrate on reinforcing the barium titanate's microstructure with a mechanically hard phase to improve grain size, strength, hardness and fracture toughness. A typical example of such a hard phase is alumina (Al₂O₃).

From the microstructural point of view, the reinforcing alumina phase can be located in barium titanate as particles (grains) or in the form of layers. The particle composites are studied mainly in terms of improved hardness, Young's modulus, and gradually decreasing mean grain size with increasing content of alumina at acceptable piezoelectric properties [3-6]. On the other hand, the composites containing individual layers of barium titanate and alumina provide interesting results about the development of hardness and Young's modulus through the interface between layers, internal stresses, and crack propagation aiming at the final application as ceramic harvesters [7-9].

Although a few articles do not report the creation of new phases during the sintering process when barium titanate and alumina are mixed together [4,10,11], the majority of literary sources point to ongoing reactions to form new intermediate phases in particle composites [3,5,6,12-15] as well as reaction zones in layered composites [7-9]. Depending on the concentration of alumina, chosen fabrication technique, and the sintering conditions (temperature, heating rate, dwell time, pressure, etc.), the most frequently reported phases are BaAl₂O₄, BaAl₁₂O₂₀, BaAl_{13,2}O_{20,8}, BaTi₂Al₃O₁₀, Ba₄Ti₁₀Al₂O₂₇, and dominant BaTiAl₆O₁₂ [3,5,6,8,9,12-15]. Unfortunately, very little information is known about these phases, although they certainly have significant positive or negative effects on the final properties of the prepared composites.

For example, considering BaTiAl₆O₁₂ phase, Guha et al. [16] reported in 1976 petrographic and X-ray examinations of a sintered mixture containing stoichiometric composition BaO:TiO₂:3Al₂O₃ showing only one phase of BaTiAl₆O₁₂ stable at the solidus temperatures having tetragonal symmetry and densities of 3.84 g/cm³ (measured) and 3.88 g/cm³ (calculated).

The authors also claimed that BaTiAl₆O₁₂ can be prepared by solid-state reaction from appropriate proportions of BaTiO₃ and Al₂O₃. Four years later, Guha [17] introduced a ternary diagram in the system BaO-TiO₂-Al₂O₃ at 1200 °C visualising the BaTiAl₆O₁₂ phase. Lately, the works of Cadée and Ijdo [18] and Fallon et al. [19] specified that BaTiAl₆O₁₂ was found to have orthorhombic symmetry instead of the reported tetragonal symmetry. Based on our best knowledge, we found only a recent work by de Pablos-Martin et al. [20] where the fluorescence of BaTiAl₆O₁₂, serving as a bonding layer between two sapphire substrates, was presented. Therefore, fundamental information about various properties of BaTiAl₆O₁₂ is still missing in the literature.

This study deals with BaTiAl₆O₁₂ ceramics as an important product arising in composites based on BaTiO₃/Al₂O₃. The properties of both Al₂O₃ and BaTiO₃ are thoroughly described in the literature, but information on the properties of BaTiAl₆O₁₂ is missing. Therefore, the effect of BaTiAl₆O₁₂ on the final properties of such composites is unclear. This paper aims to examine in detail the microstructural, mechanical, electrical and optical properties of BaTiAl₆O₁₂ and discuss them in relation to the materials from which it was synthesised. This will enable better understanding of characteristics of composite materials containing this phase.

Experimental

Preparation route

BaTiAl₆O₁₂ was prepared by mixing tetragonal barium titanate (Nanografi, Turkey) with alumina (Taimei, Japan) in an appropriate molar ratio to get the target stoichiometry after thermal treatment. The powder was milled in the planetary ball mill (Netzsch, Germany) for 30 min using deionised water as a solvent and 5 mm tetragonal zirconia balls as milling elements. The milled powder was dried for 24 h at 50 °C and then milled again in agate mortar.

The powder was uniaxially pressed in 30 mm die at 50 MPa. Then the pellet was cold isostatically pressed at 300 MPa followed by annealing at 800 °C to obtain a green body for high-temperature dilatometry. Spark plasma sintering (SPS, Dr. Sinter 615, Fuji, Japan) was used to consolidate the powder into a disc shape using a graphite die with a 30 mm diameter. The solid-state reaction took place at a sintering temperature of 1450 °C with 5 min dwell time using heating rate of

100 °C/min, cooling rate of 50 °C/min and applied pressure of 50 MPa.

Analyses

High-temperature dilatometry (L70/1700, Linseis, Germany) was applied to identify temperature intervals of phase changes during sintering and the coefficient of thermal expansion (CTE). The thermal regimes were set at 1450 °C with 60 min dwell time (heating and cooling rates of 10 °C/min) and 500 °C without dwell (heating and cooling rates of 1 °C/min), respectively. The density of the sample was measured using the Archimedes method (ISO 18754). The phase composition of the sample was analysed using the SmartLab 3kW X-ray diffractometer (XRD, Rigaku, Japan). A piece from the sintered disc was cut, mounted onto the epoxy resin, ground, and polished on progressively finer diamond abrasives down to 1 µm. The polished surface was used for microstructural analysis using an SEM (Lyra 3 XMU, Tescan, Czech Republic) equipped with an EDS Ultimmax detector (Oxford Instruments, UK) and an EBSD Symmetry camera (Oxford Instruments, UK). The Aztec version 6.1 and Aztec Crystal version 3.1 (Oxford Instruments, UK) were used to analyse chemical composition and crystallography. A set of EBSD maps where the grain boundaries detection limit was set to an angle of 15° was used to obtain grain size distribution. The weighed area grain size frequency histogram was constructed based on more than 1750 grains. Mean grain size based on equivalent diameter and grain aspect ratio from major and minor fitted diameter was determined. Correction to the grain size to 3D was not applied.

Mechanical testing

To acquire indentation elastic modulus E_{IT} and Vickers hardness HV , the indentation techniques were used. Instrumented hardness was measured using a mechanical testing machine equipped with an indentation unit (Z2.5/ZHU0.2, Zwick/Roell, Germany) at 0.98–49.03 N loading. As multiple indentations can be performed on a single sample, more than ten valid measurements for statistical analysis were acquired for each load applied.

The Young's modulus E_{IET} , shear modulus G_{IET} , and consequently calculated Poisson's ratio were determined on the sintered disc of 30 mm in diameter and thickness of 1.6 mm by an impulse excitation technique using RFDA Professional (IMCE, Belgium) equipment at room temperature and air atmosphere. Elastic characteristics were determined from flexural and torsional resonant frequencies, disk geometry and density following the ASTM E1876 (ASTM C1259) standard [21,22].

All test specimens necessary for flexural strength and fracture toughness determination were cut from the sintered disk using a precise diamond saw Brillant 220 (ATM GmbH, Germany) and ground down to 10 µm diamond abrasive to eliminate cutting defects for the fracture toughness and down to ¼ µm for bending bars. The bending bars were also chamfered at the tensile side to eliminate corner stress concentration. The chevron notch was machined into the bars using a 0.15-mm-thick diamond cutting wheel.

Flexural strength was determined on test specimens loaded in the three-point bending configuration with a span of 8 mm. The nominal test specimen dimensions were predetermined by the disk thickness and were 2 mm × 2.5 mm × 10 mm. The flexural strength was determined from the fracture force when loaded using a universal electromechanical testing system (Instron 8862, UK) equipped with a load cell (HBM, Germany) of 500 N capacity. Similarly, using the same testing machine, the fracture toughness was determined on notched test specimens with a cross-section of 2.5 mm × 2 mm in size in a three-point bending configuration with a span of 10 mm. The chevron-notched beam method (CNB; ČSN EN 14425-3 for ceramics) was used to determine fracture toughness values $K_{Ic, cnb}$ calculated from the specimen's geometry, maximum of applied force and compliance function calculated via the slice method [23]. The details about this method and a comparison with the indentation can be found elsewhere [24,25].

Optical measurements

The photoluminescence excitation (PLE) and emission (PL) spectra were recorded at room temperature using a Fluorolog FL3-21 spectrometer (Horiba Jobin Yvon, France) in the backscattering configuration (front-face). The cw Xe-lamp (450 W) was used as an excitation source, and the luminescence signal was detected with a PPD-900 detector. The appropriate cut-off filters were used to eliminate the higher-order grating reflection artefacts in the PL spectra. The emission spectra were corrected for the spectrometer optics and the excitation lamp response. The sample surface was examined by X-ray photoelectron spectroscopy (XPS) using Nexsa G2 XPS Surface Analysis System (Thermo Scientific).

Electrical measurements

Dielectric properties were measured by Alpha-A High Performance Modular Measurement System (Novocontrol, Montabaur, Germany) in ZGS Active Sample Cell. The sample for this measurement was in the shape of a disc with a diameter of 12 mm and a thickness of 1 mm. A given amount of silver paste was applied to the sample. Then dielectric properties were measured at room temperature in a wide frequency range from 10 mHz to 1 MHz.

Results and discussion

Dilatometric measurements and XRD analysis

Fig. 1 shows the dilatometric record of the in situ conventionally sintered green body composed of barium titanate and alumina in the dilatometer. The dilatometric curve reveals that the compacted mixture is stable up to 1100 °C having no significant shrinkage. However, in the temperature range between 1100 °C and 1450 °C, sintering shrinkage occurs accompanied by two significant events associated with phase changes as a result of the solid-state reaction. The phase transformations begin at 1154 °C and 1314 °C, respectively. To explore phase evolution during sintering, three samples were

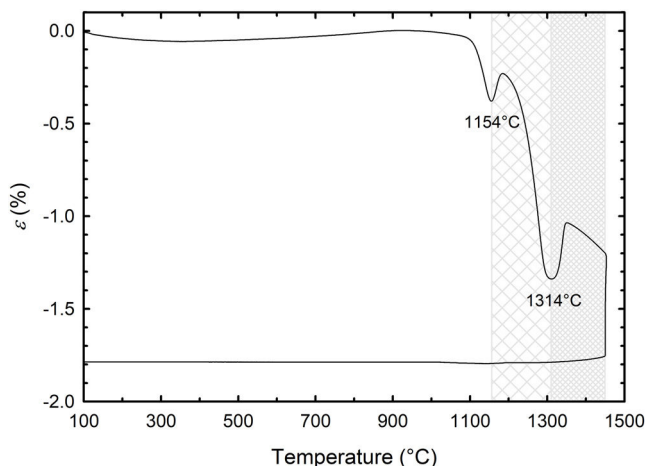


Fig. 1 – Sintering shrinkage of the conventionally sintered mixture of tetragonal barium titanate and alumina.

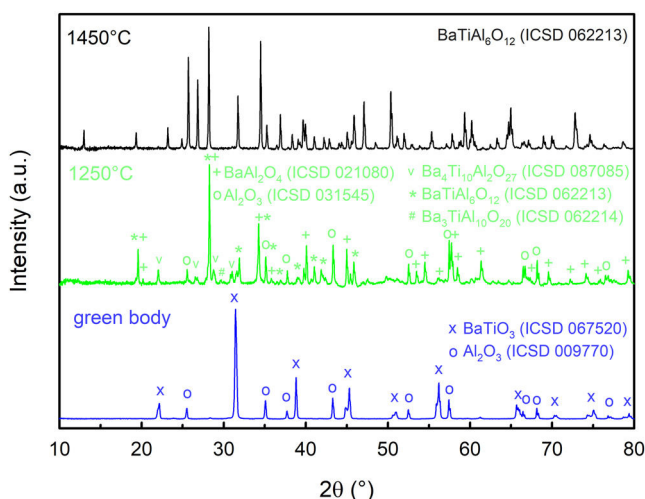


Fig. 2 – X-ray diffraction patterns of conventionally sintered samples at 800 °C, 1250 °C and 1450 °C.

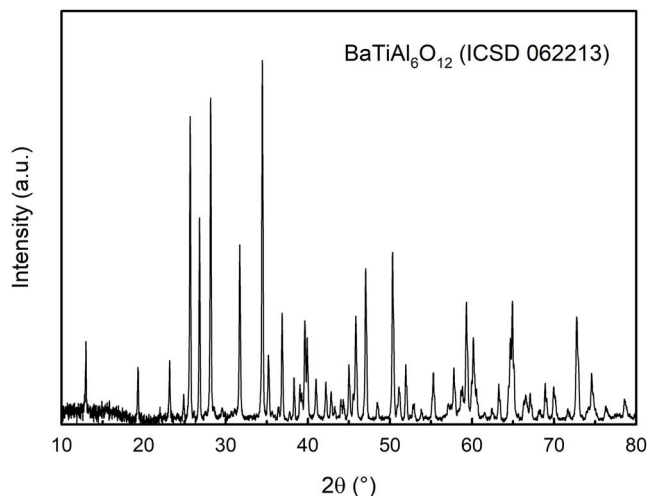


Fig. 3 – X-ray diffraction pattern of sample sintered using SPS.

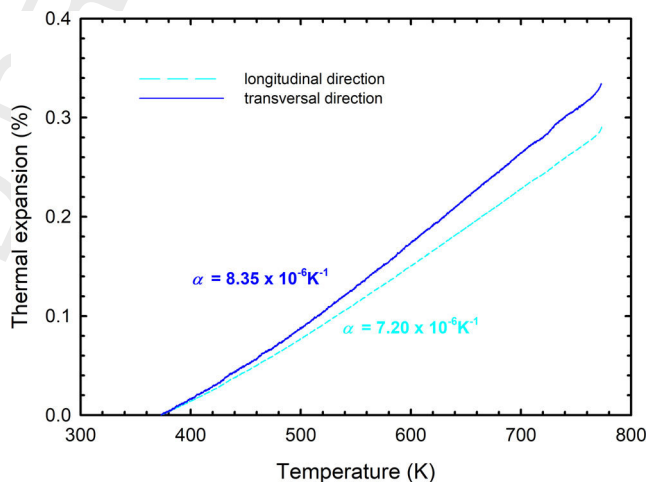


Fig. 4 – Cooling parts of dilatometric curves serving for calculation of CTE in the longitudinal and transversal orientation of the sample.

231 analysed using XRD. The first one was the green body, the sec-
 232 ond one was sintered at 1250 °C (in the region after the first
 233 phase transformation occurrence, see Fig. 1) and the third one
 234 was sintered at 1450 °C (in the region after the second phase
 235 transformation). The XRD analyses, given in Fig. 2, show the
 236 transformation of two distinct phases (BaTiO_3 and Al_2O_3) into
 237 BaAl_2O_4 , $\text{BaTiAl}_6\text{O}_{12}$, $\text{Ba}_4\text{Ti}_{10}\text{Al}_2\text{O}_{27}$, $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ and Al_2O_3
 238 at 1250 °C. The major phase was unreacted alumina (48 wt.%),
 239 followed by BaAl_2O_4 (27 wt.%) and other minor phases. Higher
 240 temperature (1450 °C) resulted in the transformation of all
 241 these phases to a single $\text{BaTiAl}_6\text{O}_{12}$ phase.

242 However, Fig. 1 also shows quite a small sintering shrink-
 243 age of ~1.8%, although the relative density of the green body
 244 was moderately high ($\rho_{g,b.} = 59.6\%$), indicating a low final den-
 245 sity of the conventionally pressure-less sintered sample. It
 246 was confirmed by density measurement, reaching a value of
 247 77.2%. From the practical point of view, we decided to use non-
 248 conventional sintering (SPS) at the same temperature with
 249 applied pressure to get a fully dense sample. The spark plasma

250 sintered sample reached a relative density of 99.5%. The XRD
 251 analysis of the SPS sample is given in Fig. 3. The X-ray diffrac-
 252 tion pattern comprises peaks of the $\text{BaTiAl}_6\text{O}_{12}$ phase.

253 Fig. 4 shows the cooling parts of dilatometric curves for the determi-
 254 nation of CTE. The CTE was calculated for the sample's transversal (plane of the disc
 255 base) and longitudinal (direction of applied pressure during
 256 SPS) orientation. The calculated values of CTEs in the tem-
 257 perature range between 100 °C and 500 °C were $8.35 \times 10^{-6} \text{ K}^{-1}$
 258 and $7.20 \times 10^{-6} \text{ K}^{-1}$ for transversal and longitudinal orienta-
 259 tion, respectively. The calculated CTEs of the $\text{BaTiAl}_6\text{O}_{12}$ phase
 260 are closer to the CTE of alumina ($8 \times 10^{-6} \text{ K}^{-1}$ [26]) rather than
 261 of barium titanate ($11 \times 10^{-6} \text{ K}^{-1}$ [8,27]). Calculated CTE val-
 262 ues and different slopes of dilatometric curves may seem to
 263 indicate anisotropy of the coefficient of thermal expansion of
 264 $\text{BaTiAl}_6\text{O}_{12}$. The anisotropy was found not in the grain orienta-
 265 tion but in the aspect ratio only (discussed further). However,
 266

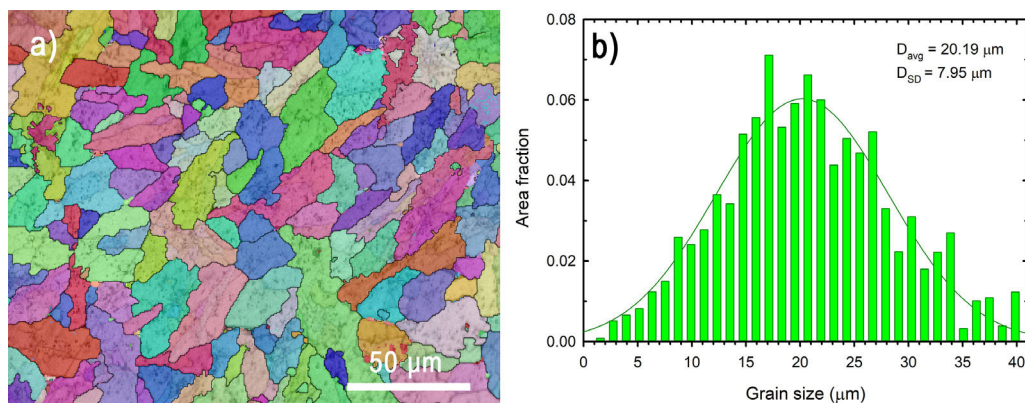


Fig. 5 – Images of (a) EBSD map and (b) grain size distribution of sample sintered using SPS.

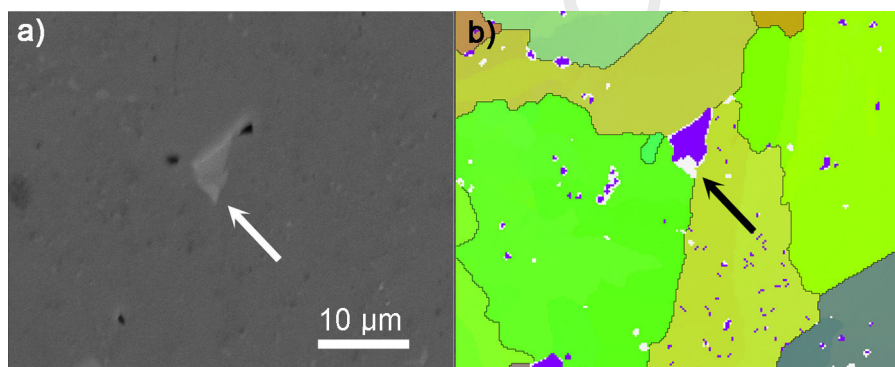


Fig. 6 – SEM images (a) and corresponding EBSD map (b) of sample sintered using SPS.

267 the generally known variance of CTE values must also be con- 293
 268 sidered. 294

269 Microstructure

270 The microstructure visualised using the EBSD detector in SEM 295
 271 is shown in Fig. 5a. The image shows rather elongated grains 296
 272 with different crystallographic orientations of the orthorhombic 297
 273 lattice. The grain growth direction preference may have 298
 274 been caused by the applied pressure during the sintering pro- 299
 275 cess. The aspect ratio of the fitted major and minor ellipse 300
 276 diameter is equal to 2.1. Grain orientation anisotropy was not 301
 277 detected based on the EBSD data. The area-weighted grain size 302
 278 distribution is plotted in Fig. 5b. The mean grain size of the 303
 279 SPS sample determined using the distribution function was 304
 280 20.19 μm . 305

281 The EBSD analysis also revealed the existence of the sec- 306
 282 ondary phase. This phase can be seen due to phase contrast 307
 283 in the SEM image in Fig. 6a and, at the same time, also on the 308
 284 corresponding EBSD map. The phase (purple area in Fig. 6b) 309
 285 was identified as monoclinic $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ localised mainly in 310
 286 the triple points of the $\text{BaTiAl}_6\text{O}_{12}$ phase. It was represented in 311
 287 the amount of 2.5% of all the phases analysed by EBSD. There- 312
 288 fore, it was not detected by XRD due to the resolution limit of 313
 289 the instrument. However, the bright grain in Fig. 6a contains 314
 290 an even brighter area marked by the white arrow in the SEM 315
 291 image and the black arrow in the EBSD map as not identified 316
 292 area. It is believed that they are the transition reaction prod- 317

ucts of incomplete transformation on $\text{BaTiAl}_6\text{O}_{12}$. Although 293
 the minor phases were analysed, we assume that their small 294
 amounts do not substantially affect the final properties of the 295
 $\text{BaTiAl}_6\text{O}_{12}$. 296

297 Mechanical properties

298 The indentation at various loading levels was conducted to 299
 obtain a set of data revealing information about the size effect 300
 of the $\text{BaTiAl}_6\text{O}_{12}$. The dependence is shown in Fig. 7 for both 301
 the Vickers hardness calculated from measured indentation 302
 depth and calculated indentation elastic modulus determined 303
 from the unloading part of loading curves. Both dependen- 304
 cies exhibit typical shapes where approximately for loads 305
 above 10 N a plateau can be identified and the hardness of 306
 the $\text{BaTiAl}_6\text{O}_{12}$ can be estimated at the level of 10 GPa. The 307
 indentation elastic modulus ranked between 187 GPa for HV0.1 308
 and 132 GPa for HV5. The load of HV5 (49.05 N) and above led 309
 to the formation of significantly large cracks but the value of 310
 hardness could not be affected by this phenomenon known 311
 for brittle materials [28]. 312

313 The elastic properties obtained by the impulse excitation 314
 technique showed slightly higher values of Young's modu- 315
 lus than the average in indentation. The calculated value 316
 from resonance frequencies was 179.4 ± 0.08 GPa which corre- 317
 sponds rather with the indentation elastic modulus obtained 318
 at lower loads applied. This finding is in good correlation with 319
 the fact that E_{IET} generally provides higher and more precious 320

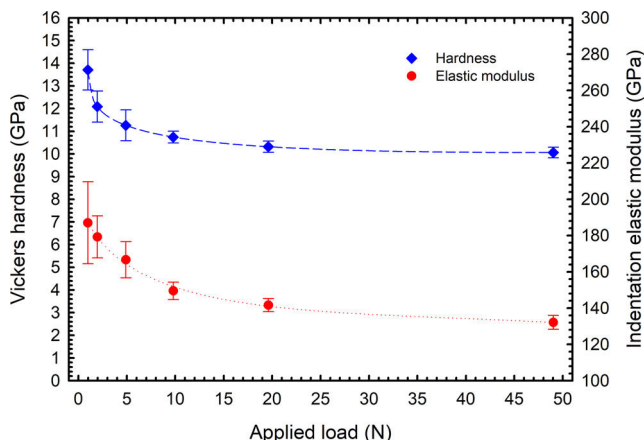


Fig. 7 – Dependence of Vickers hardness and indentation elastic modulus on the applied load.

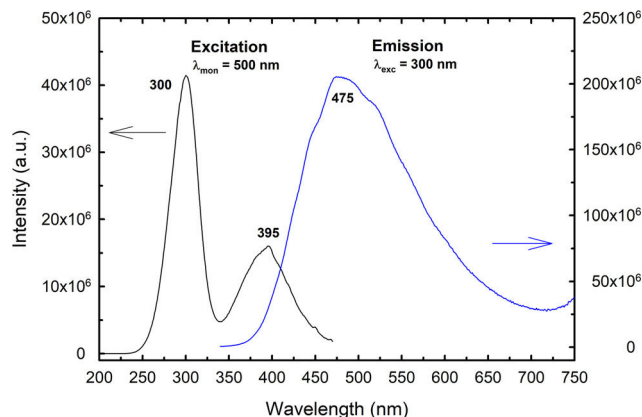


Fig. 9 – The excitation and emission spectrum of BaTiAl₆O₁₂ ceramics recorded at room temperature.

values than methods based on mechanical deformation and is rather comparable with nanoindentation [29]. The E_{IET} also allows the determination of shear modulus and the calculation of Poisson's ratio to be 69.5 ± 0.05 GPa and 0.29 ± 0.001 , respectively. Compared with the BaTiO₃, elastic properties are slightly higher but deeply below typical values for alumina [30,31].

The flexural strength determined by three-point bending was 129.9 ± 4.57 MPa, which is approximately 30% higher than typical maximal values for BaTiO₃ laying on the level of 100 MPa [30]. The fracture toughness of the BaTiO₃ is mostly determined by the indentation technique; however, some works also use standard approaches, resulting in the values oscillating around $1 \text{ MPa m}^{1/2}$ [29,32]. To compare with the BaTiAl₆O₁₂, the measured value was $1.8 \pm 0.15 \text{ MPa m}^{1/2}$, i.e., 80% higher; however, not reaching the typical value $3.6 \text{ MPa m}^{1/2}$ for alumina [33]. Generally, it can be stated that BaTiAl₆O₁₂ exhibits overall better mechanical properties than BaTiO₃; therefore, it will be beneficial when formed at the interfaces with Al₂O₃. The typical fracture surface is presented in Fig. 8, showing transgranular fracture mode on the backscattered electron mode of SEM images. The observed transgranular fracture mode indicates a strong boundary strength of adjacent grains [34]. The detailed view (see Fig. 8c) shows that the secondary phase (white grain of Ba₃TiAl₁₀O₂₀) did not change the overall fracture morphology.

Optical properties

The crystal structure of BaTiAl₆O₁₂, reported by Fallon et al. [19], consists of two types of octahedra with mixed Ti and Al occupancy and tetrahedra (AlO₄) forming a three-dimensional framework with tunnels containing barium ions. From these constituents, only the Ti-oxygen polyhedron can absorb ultra-violet light due to charge-transfer transitions as known for a large number of hosts [35,36]. The tetrahedral titanate group (TiO₄) absorbs only at wavelengths shorter than 250 nm [36], while the octahedral titanate groups (TiO₆) absorbs at longer wavelengths. Because Ti occupies only octahedral sites in BaTiAl₆O₁₂, absorption at longer wavelengths than 250 nm is expected.

Since various titanium oxidation states (mainly Ti⁴⁺/Ti³⁺) in oxide hosts may contribute to the luminescence, the sample surface was examined by XPS (figure not shown). The two prominent Ti 2p peaks originating from Ti 2p_{1/2} at 464.6 eV and 2p_{3/2} at 458.6 eV were observed in the XPS spectrum corresponding to the Ti⁴⁺-ion profile. This suggests that almost no or only negligible reduction of Ti⁴⁺ to Ti³⁺ occurs, and the Ti ions maintain the stable valence state of 4+.

The excitation (PLE) and emission (PL) spectra of BaTiAl₆O₁₂ ceramic are presented in Fig. 9. The PLE spectrum was recorded under the monitoring of the emission wavelength at 475 nm and 500 nm, respectively. The spectrum consists of two broad bands, the first most intensive band in the wavelength

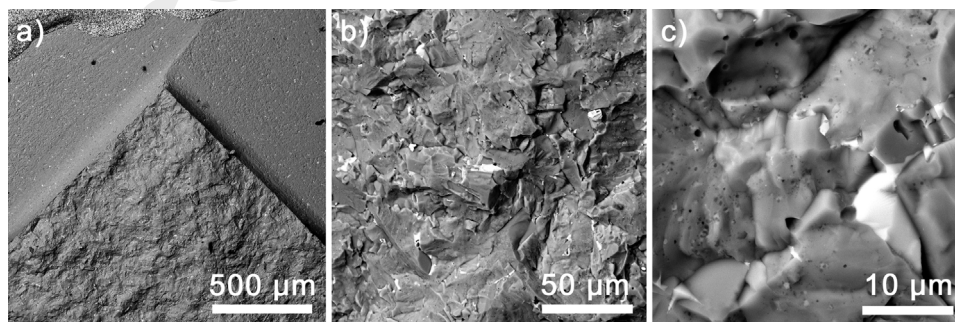


Fig. 8 – Typical example of the fracture surface of CNB specimen with increasing magnification from left to right.

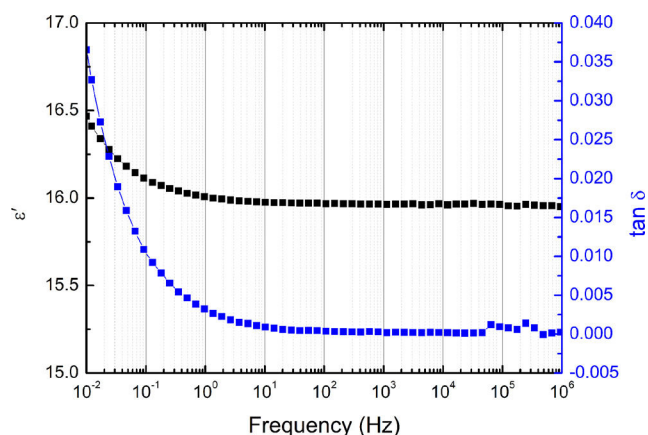


Fig. 10 – Real part of permittivity (ϵ') and dielectric loss ($\tan \delta$) vs frequency at room temperature.

range of 250–340 nm centred at about 300 nm, and the second one in the range of 340–500 nm with a maximum at 395 nm. No absorption band at around 500 nm, typical for the Ti^{3+} ions, was observed in excitation spectra. The excitation at 300 nm corresponds to $\text{Ti}^{4+}-\text{O}^{2-}$ charge-transfer transition (CT) from the 2p orbital of O^{2-} into the 3d orbital of Ti^{4+} , which is common for titanates and Ti-doped compounds [37–41]. When the ceramic was excited at this wavelength, the broad-band emission ranging between 360 and 700 nm and centred at 475 nm was observed. This emission can be attributed to the charge-transfer transition of the Ti^{4+} with the following mechanism [39–41]: $\text{Ti}^{4+} + h\nu_{\text{exc}} \rightarrow \text{Ti}^{3+} + h^+ \rightarrow (\text{Ti}^{4+})^* \rightarrow \text{Ti}^{4+} + h\nu_{\text{lum}}$. In this mechanism, an electron from the valence band is transferred to Ti^{4+} ion with the creation of Ti^{3+} and a hole in the valence band (strongly coupled electron–hole system $\text{Ti}^{3+}-\text{O}^-$), resulting in Ti^{3+} ion in the electronic excited state. Subsequently, the interaction between excited (3d) electron and lattice results in the Stokes shift and finally, this excitation is radiatively annihilated, emitting the photon around 475 nm.

The origin of the second absorption band centred at 395 nm in the PLE spectrum is not unequivocally clear, but this band is probably associated with defect sites in the structure. The excitation of $\text{BaTiAl}_6\text{O}_{12}$ ceramic in this wavelength range also leads to the visible emission between 400 and 650 nm (a bit blue shifted with a maximum at 460 nm); however, new less intensive broad-band emission appeared in the NIR range of 720–850 nm and centred at 775 nm. This implies that various defect sites may also contribute to overall luminescence in $\text{BaTiAl}_6\text{O}_{12}$.

Electrical properties

A real part of permittivity (ϵ') and the dielectric loss ($\tan \delta$) of $\text{BaTiAl}_6\text{O}_{12}$ as a function of frequency, measured at room temperature, are shown in Fig. 10. The sample evinced very low permittivity (ϵ') = 16 and dielectric loss ($\tan \delta$) < 0.0003 at a frequency 1 kHz. At a frequency range 10 mHz to 1 MHz, the ϵ' evinces the highest value of 16.5 at a frequency of 10 mHz and smoothly decreases to approximately 16, up to a frequency of 1 Hz. Then ϵ' is approximately constant at 16 up to a frequency of 1 MHz. The $\tan \delta$ shows similar behaviour. At the lowest fre-

quency of 10 mHz, the sample evinced the highest loss about 0.035. Then $\tan \delta$ drops sharply to 0.003 for a frequency of 1 Hz. Further, the losses decrease gradually to a minimal value of approximately 0.0001 with an increasing frequency.

Conclusions

$\text{BaTiAl}_6\text{O}_{12}$ was successfully prepared during the solid-state reaction of the tetragonal barium titanate and alumina mixture in an appropriate molar ratio. During thermal treatment, two events of phase changes were determined and analysed. The applied spark plasma sintering resulted in dense samples reaching the relative density of 99.5%. Coefficients of thermal expansion were calculated from the dilatometric measurements ranging from 7.20 to $8.35 \times 10^{-6} \text{ K}^{-1}$ in dependence on the sample orientation. The EBSD analysis showed elongated grains (mean grain size of 20.19 μm) with different crystallographic orientations of the orthorhombic lattice and 2.5% of monoclinic $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ phase localised mainly in the triple points of the $\text{BaTiAl}_6\text{O}_{12}$ phase. The Vickers hardness and indentation modulus were force dependent and for loads between HV0.1 and HV5 ranged between 13.7 GPa and 10.1 GPa for the Vickers hardness and between 187 GPa and 132 GPa for the indentation modulus. Young's modulus calculated from resonance frequencies was 179 GPa. The flexural strength and fracture toughness of $\text{BaTiAl}_6\text{O}_{12}$ determined by three-point bending were $129.9 \pm 4.57 \text{ MPa}$ and $1.8 \pm 0.15 \text{ MPa m}^{1/2}$, respectively. The fractographic analysis of the fracture surfaces revealed transgranular fracture mode. In the case of optical properties, the blue broad-band emission under UV excitation was observed in $\text{BaTiAl}_6\text{O}_{12}$ ceramics, which is due to the charge-transfer transition of the Ti^{4+} and defect sites. The measurement of electrical properties at room temperature showed low permittivity (ϵ') = 16 and dielectric loss ($\tan \delta$) < 0.0003 at a frequency 1 kHz.

Data availability statement

The datasets generated during and/or analysed during the current study are available in the repository (<https://doi.org/10.5281/zenodo.10609604>).

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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