Multi-Enhanced-Phonon Scattering Modes in Ln-Me-A Sites co-substituted LnMeA_{11}O_{19} Ceramics

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Authors reported an effective path to decrease the thermal conductivity while to increase the coefficient of thermal expansion, thus enhancing the thermo-physical properties of the LnMeA_{11}O_{19}-type magnetoplumbite LaMgAl_{11}O_{19} by simultaneously substituting La^{3+}, Mg^{2+}, and Al^{3+} ions with large ionic radius Ba^{2+}, Zn^{2+}, and Ti^{4+}, respectively. The mechanism behind the lowered thermal conductivity was mainly due to the multi-enhanced-phonon scattering modes in Ln-Me-A sites co-substituted LnMeA_{11}O_{19} ceramics. These modes involve the following four aspects, namely, point defect mechanism, the intrinsic scattering in the complex crystal cell and materials with stepped surface to localize phonon vibrational modes, as well as nano-platelet-like structure to incorporate additional grain boundary scattering. This study provides novel thoughts for promising candidate materials of even lower thermal conductivity for the next generation thermal barrier coatings.

Thermal barrier coatings (TBCs) have attracted extensive interest owing to their wide applications in the areas of coat transition pieces, combustion lines, first stage blades and vanes, as well as hot-path components of gas turbines. In addition to high melting points, absence of phase transformation from room temperature to the operating temperature, chemical inertness, low sintering rate and thermal expansion perfectly matching the substrate, low thermal conductivity is the most valuable characteristics to be considered. The total theoretical thermal conductivity of polycrystalline ceramics is simply the sum of the followed two terms 1-3:

\[
\kappa = \kappa_p + \kappa_r = \frac{1}{3} \left[ C_p \rho v_m + \frac{16}{3} \pi n^2 T^3 l_p \right]
\]  

where \( \kappa_p \) and \( \kappa_r \) are the thermal conductivities contributed by vibrations and radiation, respectively, \( C_p \) is the specific heat capacity at constant volume, \( \rho \) is the density of the material, \( v_m \) is the mean velocity of phonons in the material, \( l_p \) is the phonon mean free path, \( \sigma \) is Stefan Boltzmann’s constant \((5.67 \times 10^{-8} \text{ W m}^{-2} \text{K}^{-4})\), \( n \) is the refractive index of the material, \( T \) and \( l \) are the thermodynamic temperature (K) and photon mean free path, respectively. The specific heat capacity at constant volume for any crystalline solids at a value of \( 3Nk_B \approx 25 \text{ J mol}^{-1} \text{K}^{-1} \) above the Debye temperature. Therefore to lower the thermal conductivity in TBCs ceramics, the main approaches are to lower \( \rho, v_m \) or \( l_p \). The total phonon mean free path, in TBCs ceramics, is primarily defined by:

\[
l^{-1} = \sum \left[ l_{\text{vac}}^{-1} + l_{\text{gb}}^{-1} + l_{\text{po}}^{-1} + l_{\text{ls}}^{-1} \right]
\]  

where \( l \) is the intrinsic mean free path of phonons due to the difference among ion masses, \( l_{\text{vac}} \), \( l_{\text{gb}} \), \( l_{\text{po}} \) and \( l_{\text{ls}} \) are the mean free path of phonons contributed by vacancies, grain boundaries, point defects and layered microstructures, respectively. The designs to reduce \( l \) have been engineered on several types of oxide ceramics, intermetallic compounds or metal chalcogenides (e.g. La_{2}Zr_{2}O_{7}, 7-8YSZ, BaZrO_{3}, W/Al_{2}O_{3}, YbTe-PbSnS_{2}) by separately introducing point defects, vacancies, complex crystal structures, nanosized grains and layered microstructures. However, there is insufficient research into realizing above-mentioned scattering mechanisms jointly working in one TBCs material system, and materials meeting these requirements are not easily synthesized in the laboratory.

Recently, some researchers have reported experimentally that nano-grain boundaries11,12, point defects13 and layered microstructure14 play important roles in enhancing the phonon scattering. Focusing on the role of...
combined phonon scattering mechanisms on the thermal conductivity, we note that LnMeA11O19\(^{14-17}\) (Figure S1, Supplementary information) has been proposed as one of promising candidates for the next generation thermal barrier coatings\(^{14}\). However, doping-free LaMgAl\(_{11}\)O\(_{19}\) still shows relatively high thermal conductivity, rendering it harder to achieve smaller phonon mean free path. While introducing point defects has been proved to be an effective approach to reduce thermal conductivity of materials with exceptionally low \(\kappa\). Furthermore, multi-sites-doping is a successful strategy to introduce multi-sites distortion and disorder with mass and strain fluctuations. In addition, smaller grain size resulting in a higher number of grain boundaries in the heat path adds additional thermal resistance to the polycrystalline solid phase. Therefore, it is significantly attractive to evaluate and characterize the thermo-physical properties of Ln-Me-A sites co-substituted LnMeA11O19 ceramics with nanosized grains and thereby to seek a novel thought to further lower thermal conductivity.

In this study, we optimized the \(\kappa\) of the LnMeA11O19-type magnetoplumbite LaMgAl\(_{11}\)O\(_{19}\) by simultaneously substituting La\(^{3+}\), Mg\(^{2+}\) and Al\(^{3+}\) ions with large ionic radius Ba\(^{2+}\), Zn\(^{2+}\) and Ti\(^{4+}\) (Table S1, Supplementary information), respectively, and introducing nanostructure and layered microstructures through citric acid sol-gel route\(^{18}\) and spark plasma sintering technique\(^{19}\). A better understanding of the influences of point defects, nano-grain boundaries and layered structures on thermo-physical properties is obtained by combining experimental results with the calculated minimum thermal conductivity using Clarke’s model\(^{20,21}\). The results demonstrate that the thermal conductivities of La\(_{1-x}\)Ba\(_{x}\)Mg\(_x\)Al\(_{11-x}\)Zn\(_x\)O\(_{19}\) (LBMZATO, \(x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5\)) ceramics are exceptionally low, close to the predicated minimum thermal conductivities, which verifies that the inter-atomic spacing-sized phonon mean free paths are responsible for the point-defect scattering, high-density grain-boundary scattering, and localized phonon vibrational modes by layered crystal structure. More importantly, the coefficients of thermal expansion of LBMZATO ceramics at 1073–1273 K also show a remarkable improvement with the increased Ba\(^{2+}\), Zn\(^{2+}\) and Ti\(^{4+}\) content fraction, reaching the maximal value of 11.39 × 10\(^{-6}\) K\(^{-1}\) at 1273 K, which is close to the CTE of 7–8 \(\times 10^{-6}\) K\(^{-1}\) of yttria-stabilized zirconia (YSZ) system at the elevated temperature\(^{22}\). These conclusions suggest that LBMZATO ceramics are promising candidates for advanced thermal barrier coatings applications.

**Results**

According to the XRD patterns (Fig. S2), all the obtained LBMZATO ceramics were comprised of pure magnetoplumbite LaMgAl\(_{11}\)O\(_{19}\) phase. Increasing Ba\(^{2+}\) + Zn\(^{2+}\) + Ti\(^{4+}\) doping fraction leads to a shift of the X-ray spectra to lower 20 values (Fig. S3). The refined cell parameters of LBMZATO (with 0.0 ≤ \(x \leq 0.5\)) are listed in Table S2. The sites formation energy calculation of invasion ions and cell parameters of LBMZATO (with 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) ceramics are obtained: \(\text{Table S1, Supplementary information}\), respectively, and finite solid solutions are calculated by material studio (Tab. S3). The exact composition of the materials were determined by X-ray fluorescence spectrometry (XRF, Tab. S4) and X-ray photoelectron spectroscopy (XPS, Tab. S5 and Fig. S4). It can be concluded that Ba\(^{2+}\), Zn\(^{2+}\) and Ti\(^{4+}\) have completely entered the sites of La\(^{3+}\), Mg\(^{2+}\) and Al\(^{3+}\), respectively, and finite solid solutions have formed. For the magnetoplumbite LaMgAl\(_{11}\)O\(_{19}\), the dependence between parameters of LBMZATO and Ba\(^{2+}\), Zn\(^{2+}\) and Ti\(^{4+}\) doping fraction was approximately consistent with the Vegards’ law\(^{23}\), which displays a linear relationship between crystal structural parameters and composition variation. The smallest platelike crystallites in this material were 35 nm in thickness, as clearly evidenced in the typical SEM image of LaMgAl\(_{11}\)O\(_{19}\) without doping (Figure 1a). Figure 1b is the typical TEM morphology of LaMgAl\(_{11}\)O\(_{19}\) showing uniformity of phase composition. The selected area electron diffraction (SAED) pattern (Figure 1c) confirms that LaMgAl\(_{11}\)O\(_{19}\) possesses a magnetoplumbite-type hexagonal crystal structure. High resolution TEM (HRTEM) image (Figure 1d) with electron beam parallel to [1 1 2] and Ti\(^{4+}\) direction also revealed the crystalline structure and the smooth surface with a (1 1 00) plane.

As observed in the high-magnification SEM and TEM (Figure 2a,b), stepped crystal grains with ~50 nm height and ~100 nm width exist in the sample. Figure 2 (c) is a high-magnification atomic resolution image in [0001] direction, which reveals two parts that are separated by one dashed line. Figure 2d is the reduced FFT (Fast Fourier Transform) from region B in Figure 2c, including two clear step-like surfaces. The electron diffraction patterns of the upper and lower parts show identical magnetoplumbite-type hexagonal crystal structure. Detailed analysis showed that the lower and upper parts were well matched with each other because both include (004) and (006) lattice planes, which indicates that the border line between the lower and upper parts is coherent interface.

The thermal diffusivities and specific heat capacities in the range 293–1273 K are illustrated in Fig. S5 and Fig. S6 (Tab. S6), respectively. The thermal conductivities initially decrease with increasing \(x\), reaching their lowest values at \(x = 0.5\). The thermal conductivity of LBMZATO decreases with increasing temperature from room temperature to 800 °C (Figure 3). Due to thermal radiation at high temperatures, thermal conductivity becomes less sensitive to composition variation, instead, it rises slightly. The \(T^{-1}\) temperature-dependent thermal conductivity for LBMZATO suggests a dominant phonon conduction behavior in most inorganic non-metallic materials. Thermal conductivities of LBMATO ceramics are obviously lower than 8YSZ, especially for La\(_{0.5}\)Ba\(_{0.5}\)Mg\(_{0.5}\)Zn\(_{0.5}\)Al\(_{10.5}\)Ti\(_{0.5}\)O\(_{19}\), whose thermal conductivity values are 1.51 ~ 1.67 W·m\(^{-1}\)·K\(^{-1}\) from room temperature to 1000 °C. The coefficients of thermal expansion of LBMZATO (with 0.0 ≤ \(x \leq 0.5\)) solid solution are plotted in Figs. S7–8. CTE rises with the increasing Ba\(^{2+}\), Zn\(^{2+}\) and Ti\(^{4+}\) fraction, which exhibits a composition dependence similar to the reverse composition dependence of the thermal conductivity.

**Discussion**

An inter-atomic spacing-sized phonon mean free path means that the strongest scattering occurs in the crystal cell and corresponds to the minimum thermal conductivity as reported by Clarke\(^{21}\). In light of Debye’s phonon gas theory, thermal conduction in dielectric solids can be considered as the transport of phonons carrying energy, and the thermal conductivity of materials is then represented in another form equivalent to \(\kappa = \alpha \cdot C\nu_m \rho\), by the relation\(^{22}\):

\[
\kappa' = \frac{1}{3} C\nu_m \cdot \rho_i \cdot l, \tag{3}
\]

where \(C\nu_m\), \(\nu_m\) and \(l\) represent the heat capacity per unit volum, the average speed of sound in the materials and the phonon mean free path, respectively. By combining Eqs. (3) and the relation \(C\nu = C\rho \cdot \nu_m\), the phonon mean free path can be expressed as:

\[
l = \frac{2\nu_m}{C\nu} \tag{4}
\]

where \(\nu\) is characterized by the laser flash system (Netzsch LFA 427, Germany) from room temperature up to 1273 K in an argon atmosphere. For each temperature, three measurements were made to obtain the mean value of thermal diffusivity. The average speed of sound \(\nu_m\) is determined by the relation:

\[
\nu_m = \left[ \frac{3(\nu_0 \nu_i)}{2\nu_0^2 + \nu_i^2} \right]^{1/3} \tag{5}
\]

Combining Eqs.(4) and (5), the phonon mean free path can be obtained:
where $v_l$ and $v_t$ represent longitudinal and transverse sound speed, respectively.

The phonon mean free path of LBMZATO solid solutions as a function of temperature is plotted in Fig. 4. The phonon mean free paths of LBMZATO are nearly temperature-independent above 873 K (equal to Debye temperature of LBMZATO), which agrees with the typical behavior of inorganic materials. The phonon mean free paths of LBMZATO ceramics vary between 0.18 and 0.34 nm in the range from room temperature to 1000°C. This confirms that the phonon mean free path is smaller than parameters ($a = b = 5.5920$ Å, $c = 21.9650$ Å) and approaches the inter-atomic spacing. The distance between the $\text{Al}^{3+}$ cation and $\text{O}^{2-}$ anion in $\text{AlO}_3$ hexahedron is 1.74 Å.

Clarke evaluated a formula based on the minimum thermal conductivity according to the phonon mean free path equal to the inter-atomic spacing:

$$I = 3\alpha/3^{1/3}(\frac{1}{v_l} + \frac{2}{v_t})^{1/3}$$

(6)

where $v_l$ and $v_t$ represent longitudinal and transverse sound speed, respectively.

The phonon mean free path of LBMZATO solid solutions as a function of temperature is plotted in Fig. 4. The phonon mean free paths of LBMZATO are nearly temperature-independent above 873 K (equal to Debye temperature of LBMZATO), which agrees with the typical behavior of inorganic materials. The phonon mean free paths of LBMZATO ceramics vary between 0.18 and 0.34 nm in the range from room temperature to 1000°C. This confirms that the phonon mean free path is smaller than parameters ($a = b = 5.5920$ Å, $c = 21.9650$ Å) and approaches the inter-atomic spacing. The distance between the $\text{Al}^{3+}$ cation and $\text{O}^{2-}$ anion in $\text{AlO}_3$ hexahedron is 1.74 Å.

Clarke evaluated a formula based on the minimum thermal conductivity according to the phonon mean free path equal to the inter-atomic spacing:

$$k_{\text{min}} = 0.87k_B\Lambda^{2/3} \frac{m^{2/3} \rho^{1/6} E^{1/2}}{M^{7/3}}$$

(7)

where $k_B$ is Boltzmann’s constant, $N_A$ is the Avogadro number, $m$ is number of atoms per molecule, $\rho$ is the density, $M$ is the molecular mass, and $E$ is the Young’s modulus. Values of $k_{\text{min}}$ were calculated by Eq.(7) and the relationship between $k_{\text{min}}$ and composition was also plotted in Fig. 3. The measured thermal conductivity of LBMZATO was close to the calculated minimum thermal conductivity, which means that the phonon mean free path may be as small as the inter-atomic spacing.

With the aid of the Debye model, the mechanism behind the such low thermal conductivities in LBMZATO solid solution can be well understood. The thermal conductivity in the form of the Debye model could be given by:

$$k = k_B \frac{\alpha_T}{h} \left(\frac{k_B T}{\hbar}\right)^3 \int_{0}^{\Theta_D/T} \frac{x^4 \varepsilon^2}{T_c (e^x - 1)^2}dx$$

(8)

where $x = \hbar \omega/(k_B T)$ is a dimensionless quantity and $T_c$ is the phonon scattering relaxation time. The following processes are assumed to limit the flow of phonons: grain-boundary scattering, point-defect scattering, phonon-phonon Umklapp scattering, stacking faults and dislocation. Therefore the combined resistive $T_c^{-1}$ (reciprocal of relaxation time) can be defined:

$$T_c^{-1} = T_s^{-1} + T_p^{-1} + T_g^{-1} + T_u^{-1} + T_{\text{Dis}}^{-1} + T_{\text{Stepped}}^{-1}$$

where $T_s^{-1}$, $T_p^{-1}$, $T_g^{-1}$, $T_u^{-1}$, $T_{\text{Dis}}^{-1}$ and $T_{\text{Stepped}}^{-1}$ are the resistives contributed by grain-boundary scattering, point-defect scattering, phonon-phonon Umklapp scattering and grain-boundary scattering, stacking faults, dislocation and stepped surface, respectively. $L$ is the typical grain size and $A$, $B$, $C$, $D$ and $E$ are adjustable parameters for phonon scattering from point-defect, Umklapp phonon-phonon interactions, stacking faults, dislocation, and displacement layers respectively. In this work, authors suppose that the main sources of thermal...
resistance are represented by plate-like grain boundary\textsuperscript{31,32} and point-defect\textsuperscript{33} as well as stepped surface\textsuperscript{10,34} in the crystal. The grain boundary term has the least effect on the phonon mean free path in conventional coarser-grained materials. However, the phonon mean-free-path may be strongly affected by the additional phonon scattering at interfaces that is induced by grain-size reduction\textsuperscript{35,36}. In our study, it is hypothesized that nanocrystalline materials offer the potential of limiting thermal conductivity by incorporating plate-like grain boundary scattering as an extrinsic phonon-scattering phenomenon. The expression for relaxation time due to grain boundary scattering process has been given by Casimir\textsuperscript{37}:

\[
t_{B}^{-1} = \frac{\nu_{m}}{L},
\]

where \(\nu_{m}\) is the mean velocity of phonons in the material, \(L\) mean grain size. Due to enhanced phonon scattering at high-density grain boundaries (Fig. 5a), the specimens synthesized by citric acid sol-gel technique showed a reduction (~13\%) in thermal conductivity compared with the conventional solid-state with microscale grains (Fig. 5b).

The resistive contributed by point-defect scattering can be given by Klemens as\textsuperscript{38}:

\[
t_{D}^{-1} = A\omega_{D}^{3} = \frac{4}{\pi} \left( \frac{\delta}{\nu_{m}} \right)^{3} \Gamma \omega_{D}^{3}
\]

where \(\Gamma\) is the total imperfection parameter, which is given in Eqs.(S1–3, Supporting Information). Debye frequency \(\omega_{D}\) is given by \((6\pi^{2}v_{m}^{3}/\Omega)^{1/3}\), where \(\Omega\) is given by \(M_{A}/\rho, M_{A}\) is the average atomic mass and \(M_{A}\) of LaMgAl\textsubscript{11}O\textsubscript{19} is 3.96 \times 10\textsuperscript{-22} g.

In addition, authors consider another process of phonon scattering in LBMZATO samples to account for the resistive contributed by stepped surface \(t_{\text{Stepped}}^{-1}\)\textsuperscript{39}:

\[
t_{\text{Stepped}}^{-1} = E\omega_{D}^{3} = \frac{4}{3} \frac{1}{G_{N}u_{m}} \frac{a}{18} \omega_{D}^{3}
\]

Figure 2 | (a) The high-magnification SEM image for LBMZATO with Ba\textsuperscript{2+}, Zn\textsuperscript{2+} and Ti\textsuperscript{4+} dopant content fraction \(x = 0.3\). (b) The high-magnification transmission electron microscope (TEM) image of (a). (c) The HRTEM image taken from the red circle region A in (b). (d) The reduced FFT from region B in image (c) includes two clear step-like surfaces.

Figure 3 | Thermal conductivity as a function of temperature for fully dense LBMZATO (0.0 \(\leq x \leq 0.5\)) ceramics. The standard deviation of thermal conductivity values is within 2\% based on three independent laser flash measurements, which is smaller than the symbol in the figure.
where $G_N$ is the number of stepped surface in a crystal, $a$ is the constant. Vibrations of stepped surfaces have been studied by P. Knipp. In the proximity of a step, further reduction of atomic constant. Vibrations of stepped surfaces have been studied by P. Knipp. Authors provided a novel thought to find some new microstructure introduced in suppressing the thermal conductivity. Here the current x

Figure 4 | Phonon mean free path of LBMZATO (0.0 ≤ x ≤ 0.5) ceramics as a function of temperature.

In summary, this study on Ba$^{2+}$, Zn$^{2+}$ and Ti$^{4+}$ co-doped Lanthanum magnesium aluminate LaMgAl$_{11}$O$_{19}$ ceramics displays increased CTE and reduced thermal conductivity, which is contributed by the substantial additional point-defect scattering, plate-like grain-boundary scattering, and stepped surfaces. Point defects are effective at scattering short wavelength phonons, while plate-like nano-grains are required to scatter mid- and long-wavelength phonons effectively, high-density grain boundaries and layered microstructures can play an effective role in scattering longer-wavelength phonons. A novel thought to further lower thermal conductivity was provided by introducing multi-enhanced-phonon scattering modes in Ln- Me-A sites co-substituted LnMeA$_{11}$O$_{19}$ ceramics, namely, materials with stepped surface to localize phonon vibrational modes and point defect mechanism, as well as nano-platelet-like structure to incorporate additional grain boundary scattering. A low thermal conductivity of 1.44 ~ 1.65 W m$^{-1}$K$^{-1}$ at 1027 K qualifies the LaMgAl$_{11}$O$_{19}$ based-bulk ceramics with high CTE (~11.2 × 10$^{-6}$ K$^{-1}$, T = 1027 K) as a promising candidate for advanced thermal barrier coatings.

Methods

The series of samples were synthesized through citric acid sol-gel route over the solid solution range according to the formula La$_{1-x}$Ba$_x$Mg$_{1-y}$Zn$_y$Al$_{11-x}$Ti$_x$O$_{19}$ (LBMZATO, x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5). Details of powder processing approach used in citric acid sol-gel route are described elsewhere. The acquired powders were isostatically cold pressed, and sintered at 1500 °C for 6 h in air to obtain LBMZATO ceramics. The LBMZATO ceramics were machined into samples of 5.0 × 5.0 × 20.0 mm for CTE characterization. Finally, full dense LBMZATO ceramics were prepared by spark plasma sintering under an applied pressure of 50 MPa at 1500 °C with a constant heating rate 100 °C min$^{-1}$ to mold into pellets of ~12.7 mm in diameter and ~1.2 mm in thickness. The temperature remained at 1500 °C for 15 min and a constant vacuum pressure of 4.5 Pa was maintained throughout the entire sintering process. As the specimens were loaded into a graphite die with an internal diameter of 13.1 mm, the LBMZATO changed into black disks due to the presence of excess graphite so all of the specimens were further heated in air at 950 °C for 8 h. The phase compositions of the sintered pellets were identified by X-ray diffraction (XRD) (Bruker-D8 Advance Da Vinci) with CuKα radiation (40 mA, 40 kV) with 2θ angle range from 10 to 90°. The phase structure were identified using a Raman spectrometer (Raman, LabRAM HR800, HORIBA Jobin Yvon, France) using an argon ion laser with radiation at 633 nm, and collected across wavenumbers 400 ~ 2000 cm$^{-1}$. The signal was collected at a rate of 600 cm$^{-1}$/30 s and accumulated by triple scanning. The sound speed in each of the solid solutions was measured by an optimization processes to further lower thermal conductivity for thermal barrier coatings, such as materials with stepped surface to localize phonon vibrational modes or nano-platelet-like structure to incorporate additional grain boundary scattering.

In the proximity of a step, further reduction of atomic constant. Vibrations of stepped surfaces have been studied by P. Knipp. In the proximity of a step, further reduction of atomic constant. Vibrations of stepped surfaces have been studied by P. Knipp. Authors provided a novel thought to find some new microstructure introduced in suppressing the thermal conductivity. Here the current authors provided a novel thought to find some new microstructure.
ultrasonic reflection method with a computer controlled ultrasonic pulser-receiver (Olympus Model 5073PR, Waltham, MA, USA). The morphology and crystal structure in LBMZATO phases upon Ba\(^{2+}\) + Zn\(^{2+}\) + Ti\(^{3+}\) co-substitution were evaluated by field emission scanning electron microscopy (SEM, JSM-7601F, JEOL, Japan) and high resolution transmission electron microscopy/electron diffraction (HRTEM/ED, JEM-2010F, JEOL, Japan) techniques.

The thermal diffusivities of the samples were characterized by the laser flash system (Netzsch LFA 427, Germany) from room temperature up to \(1273\) K exposed to air, and the temperature rise at the back side is measured as a function of time with an InSb infrared detector. The front and the back surfaces of each specimen were coated with two thin layers of carbon, approximately \(10\) \(\mu\)m thick, both to ensure the laser absorption at the front surface and to standardize the absorbance of the front surface and the emissivity of the back surface of the specimen. For each temperature three measurements were made to obtain the mean value of thermal diffusivity. The error in thermal diffusivity tests is within \(\pm 2\%\). The specific heat capacitances of the solid solutions at various temperatures were calculated according to the Neumann-Kopp rule based on the reference specific heat values of La\(_2\)O\(_3\), BaO, MgO, ZnO, Al\(_2\)O\(_3\) and TiO\(_2\). The real densities of the LBMZATO ceramics were measured by Archimedes’ method. The thermal conductivity \((\kappa)\) was calculated from the measured diffusivity \((a/\text{mm}^2 \cdot \text{s}^{-1})\), the specific heat \((C_p/\text{g} \cdot \text{K}^{-1})\) and the density \((\rho/\text{g} \cdot \text{cm}^{-3})\) using the relationship:

\[
\kappa = \rho \cdot C_p \cdot a.
\]  

(14)

The thermal conductivity of the full dense solid, \(\kappa_f\), was further normalized by the formula:

\[
\frac{\kappa}{\kappa_f} = 1 - \frac{4}{3} \Phi,
\]

(15)

where \(\Phi\) is the porosity of the sintered specimen.

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