



**RESEARCH ARTICLE**

**Thermal Barrier Coating Materials Review**

**Termal Bariyer Kaplama Malzemeleri İncelemesi**

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**Abstract**

The priority technological direction of thermal protection of hot section components, basically turbine parts is the development of thermal barrier coatings (TBCs) in order to improve the operational performance of aero gas turbine engines (GTEs). The application of this coating, which can lower the surface temperature of the substrate material and have high oxidation resistance, was of great importance. The focus of this paper is on choosing TBCs with lower conductivity and longer life than coatings used in industry today and on the study of the effect of TBCs with low thermal conductivity on the longevity and performance of the GTE. Although this type of coating consists of multilayers, here only an overview of the coating materials used in their top layer is given. This review is based essentially on the thermal and mechanical properties of these materials. Although there are many oxide materials that meet the specified requirements and are considered suitable for use as a ceramic top layer in the TBC system, the most promising one was selected. Compared to traditional TBC systems, it is a pyrochlore type oxide with very low thermal conductivity, high thermal stability, and some other advantages - Lanthanum zirconate ( $\text{La}_2\text{Zr}_2\text{O}_7$ , LZ).

**Keywords:** Aero Gas Turbine Engine, Thermal Barrier Coating, Top Coat, Novel Ceramics, Thermal and Mechanical Properties.

**Öz**

Bilindiği gibi, uçak gaz türbini motorlarının (GTM) performans özelliklerinin iyileştirilmesinin ana yönlerinden biri, yanma odasının ve gaz türbinlerinin elemanları için termal (ısı) bariyer kaplamalarının (TBK) geliştirilmesidir. TBK'nin kullanımı, alt tabaka malzemesinin yüzey sıcaklığının azaltılmasını mümkün kılar ve oksidasyona karşı iyi bir direnç sağlar. Bu özellik gaz türbin motorunun güvenilirliğini sağlamak için büyük önem taşır. Bu makale, günümüzde endüstride kullanılan kaplamalara göre daha düşük iletkenliğe ve daha uzun işletim ömrüne sahip TBK'lerin seçilmesi konusunu ele almaktadır. Düşük ısı iletkenliğe sahip TBK'nin, gaz türbin motorlarının dayanıklılığı ve başarımı üzerindeki etkisi araştırılmıştır. Termal ve mekanik özelliklere dayanarak, TBK'nin üst tabakasında kullanılan malzemelerin çözümlemesi yapılmıştır. Birçok oksit malzemenin varlığına rağmen makalede, TBK sistemindeki üst seramik tabaka için en olası malzemenin seçimi açıklanmıştır. Çalışmaların sonuçları geleneksel TBK sistemleriyle karşılaştırıldığında, çok düşük termal iletkenliğe, yüksek termal kararlılığa ve bir dizi başka olumlu yönlere sahip piroklor tipi oksit (lantan zirkonat -  $\text{La}_2\text{Zr}_2\text{O}_7$ , LZ) malzemesinin kullanımının en yüksek yarara sahip olduğu gösterilmiştir.

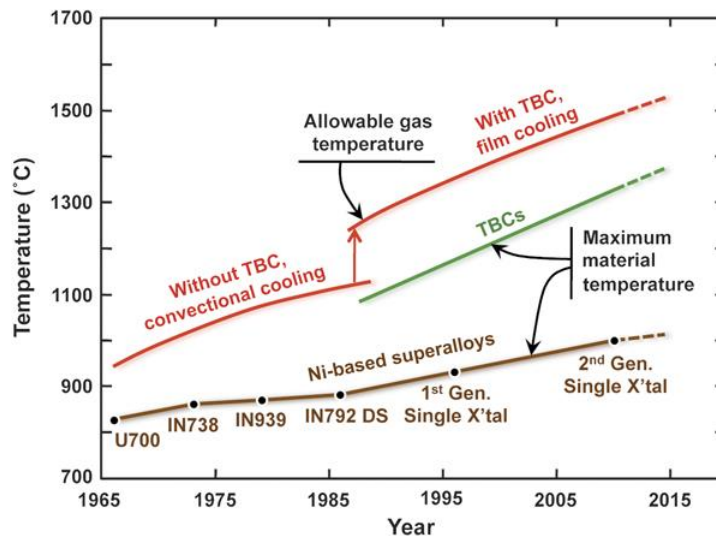
**Anahtar Kelimeler:** Aerogaz Türbin Motoru, Termal Bariyer Kaplama, Üst Kaplama, Yeni Seramikler, Isıl ve Mekanik Özellikler.

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## 1. INTRODUCTION

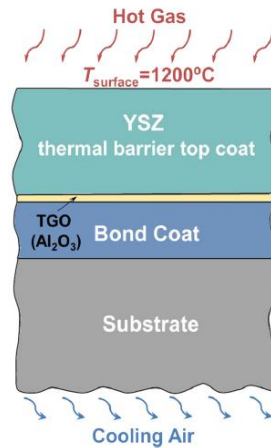
One of the most important gas turbine engine (GTE) characteristics is the temperature at the turbine inlet, and the major strategy to enhance the GTE's operating process is the formation of high gas temperatures at a turbine entry. The gas temperature at the inlet to hot section parts has already exceeded the maximum operating temperature ( $<1150^{\circ}\text{C}$ ) of nickel-based heat-resistant superalloys that are used in producing turbine blades and other parts of the hot path [1]. It is worth noting that the temperature ability of current-generation superalloys, such as cobalt or nickel-based superalloys, has been upgraded to their initial melting point, which is their maximum allowable temperature. In recent years, further enhancing their operating temperature has become difficult, and they can no longer meet the development needs of gas turbines and aero-engines. This is clearly seen in Figure 1, according to which TBC technology has significantly increased the operating temperature of GTE compared to the developments in advanced casting technology and new superalloy materials over the past few decades [2]. For this reason, the importance of TBC materials is self-evident, and researchers are actively investigating potential TBC materials to increase turbine inlet temperatures while protecting superalloys from extreme temperatures.



**Figure 1.** Growth dynamics of temperature characteristics of nickel-based superalloys and TBC materials.

Currently used TBCs are required not only to limit heat transfer through the coating, but also to protect the hot section components of GTEs from oxidation and hot corrosion, which in turn permits extending the lifespan of these components and engine efficiency at elevated service temperatures [3-7]. No other coating types composition appears able to satisfy these multifunctional requirements. Only one coating system can be used, which is TBC. Therefore, the researchers preferred to use these multilayered protective coatings, which are highly effective. These types of coatings are systems consisting of two or three or four or five separate layers, but classic TBC systems typically consist of four primary layers made of various materials with different functions: the ceramic top coat (TC) is the first layer, next intermediate layer is the thermally grown oxide (TGO), the metallic bond

coat (BC) is third layer and final is metallic superalloy substrate. Figure 2 shows the cross section of a typical TBC system [15].



**Figure 2.** Scheme of typical TBC system.

Each of these layers is made of materials with distinct characteristics and purposes. The substrate is commonly a high strength nickel- or cobalt-based superalloy capable of withstanding mechanical stress. The BC is either MCrAlY (M = Co, Ni, CoNi, NiCo, or Fe) overlay or NiPtAl diffusion coatings [5-7]. The BC provides the essential adherence of the TC to the metallic substrate, safeguards the substrate from high-temperature corrosion and oxidation, and eliminates the coefficient of thermal expansion (CTE) mismatch between the TC and the substrate. The TGO (a by product) is the result of the BC's interaction with oxygen in the air. Due to a large number of oxygen ion vacancies in ceramic coatings, oxygen transfer unavoidably occurs at high temperatures, which is accompanied by oxidation of the BC and leads to the formation of a TGO layer at the ceramic/bond coat interface. Generally,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is regarded as the ideal TGO layer because it has a very low oxygen ionic diffusivity and acts as an excellent diffusion barrier to halt further BC oxidation [3,7]. Therefore, it is very important to design the BC with a chemistry that promotes the development of an ideal TGO layer. The study of these layer materials is beyond the scope of this paper and will not be discussed further.

The TC is a key part of the TBC system, whose main function is thermal insulation and protection of the underlying material from heat flow. The most temperature reduction is achieved in this layer [3,8]. Also, this TC layer allows for internal cooling a reduction up to 6%, which corresponds to a significant increase in the efficiency of the applied component [9-11]. Therefore, when selecting oxide-containing materials for this layer, much attention is paid to their characteristics. These coatings, which are commonly made of ceramic materials, must adhere to the following merits: low thermal conductivity, CTE consistent with the metal substrate, phase stability (i.e., no phase transformation between room temperature and service temperature), low sintering rate, chemical inertness, high melting point, high fracture toughness, good strain tolerance, corrosion and erosion resistance, enhanced mechanical properties, good chemical compatibility with alumina, and good adhesion to the metal substrate [6,7,12].

This paper will discuss the status of existing top coat materials of TBCs, focusing on the main factors influencing their effectiveness.

## 2. REVIEW METHODOLOGY

The literature review involves a detailed investigation of the oxide materials used in the top layer of thermal barrier coatings with particular emphasis on their high temperature performance. High-temperature performance means their protection from thermal and mechanical effects. This review is based on coating materials that meet the specified requirements and are compatible with the properties of the BC layer/substrate. Studying the mechanical and thermal properties of pyrochlore, perovskites hexaaluminate, rare earth tantalates/niobates, and high-entropy oxide materials, and in the next step, choosing an oxide material with low thermal conductivity and high coefficient of thermal expansion from them is designed.

## 3. CERAMIC TOP COAT MATERIALS

There are few materials suitable for high-temperature TBCs. Figure 3 provides an overview of the various described types of TC materials illustrated by the corresponding thermal conductivity values depending on the CTE [13].

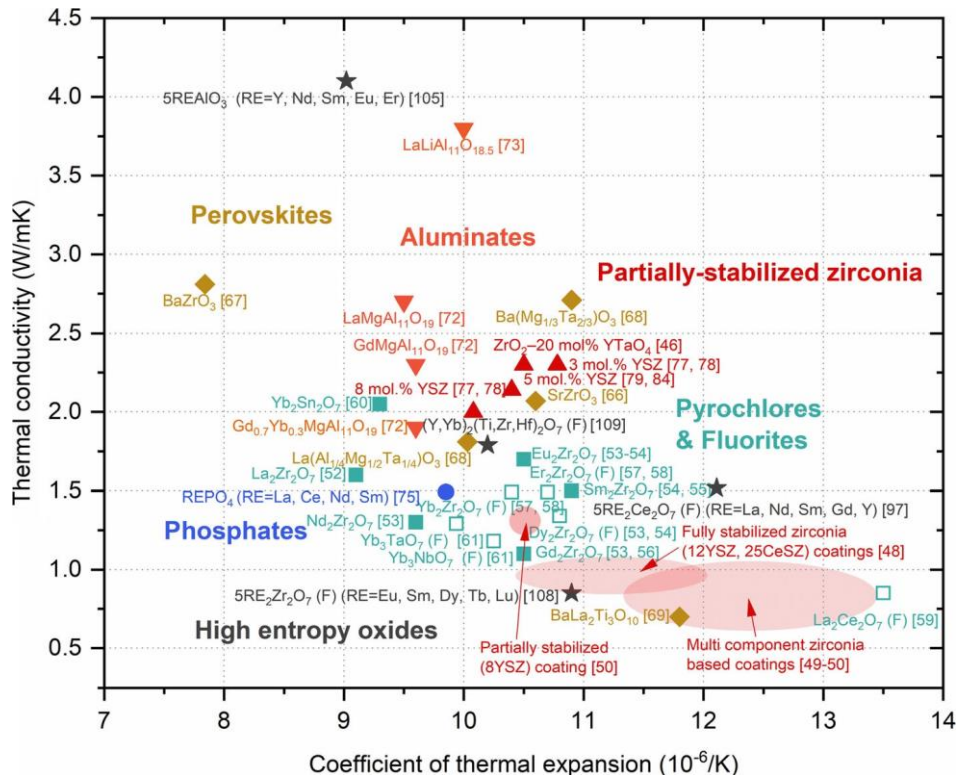


Figure 3. The thermal conductivity and coefficient of thermal expansion (CTE) of several TC candidates.

Table 1 summarizes many properties of some ceramic materials that can be used in the top layer of TBC systems that provide many of the characteristics listed above.

**Table 1.** Summary of top coat material properties.

Material	Properties		
	Thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$	Thermal expansion coefficient, $10^{-6} K^{-1}$	Temperature range, °C
YSZ	~2.3	~11	1000
Re <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> (Re=La, Eu, Sm, Nd, Gd)	~1.1-1.7	9.1-10.4	700-1000
LZ doped with Nd, Eu, Gd	~0.9	~9.2 (at 1200°C)	up to 800
(Gd <sub>1-x</sub> Yb <sub>x</sub> ) <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> (x = 0,0.1,0.3,0.5,0.7)	0.88-1.00	11.8-13.0 (at 1200°C)	1400
Gd <sub>2</sub> (Zr <sub>0.8</sub> Ti <sub>0.2</sub> ) <sub>2</sub> O <sub>7</sub>	-	~11.8 (at 1000°C)	-
(La <sub>0.5</sub> Yb <sub>0.5</sub> ) <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	0.85 (at RT)	13.53 (at 950°C)	-
La <sub>2</sub> (Zr <sub>0.5</sub> Ce <sub>0.5</sub> ) <sub>2</sub> O <sub>7</sub>	1.14	-	-
La <sub>2</sub> (Zr <sub>0.7</sub> Ce <sub>0.3</sub> ) <sub>2</sub> O <sub>7</sub>	1.06	-	-
Gd <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>	~1.18	-	-
SrZrO <sub>3</sub>	~2.1	10.8	600-1000
Ba(Mg <sub>1/3</sub> Ta <sub>2/3</sub> )O <sub>3</sub> (BMT)	2.5	-	1100
La(Al <sub>1/4</sub> Mg <sub>1/2</sub> Ta <sub>1/4</sub> )O <sub>3</sub> (LAMT)	2.0	11.9	-
SrCeO <sub>3</sub>	1.74-2.84	9.67-10.6 (200-1300°C)	RT-800
SrCe <sub>0.7</sub> Sn <sub>0.3</sub> O <sub>3</sub>	-	12.47	1100
LaMgAl <sub>11</sub> O <sub>19</sub> (LaMA)	1.95	10.95	-
GdMgAl <sub>11</sub> O <sub>19</sub>	1.79-2.05	-	20-1000
PrMgAl <sub>11</sub> O <sub>19</sub>	-	10.91	1000
NdMgAl <sub>11</sub> O <sub>19</sub>	-	10.86	1000
SmMgAl <sub>11</sub> O <sub>19</sub>	-	10.79	1000
EuMgAl <sub>11</sub> O <sub>19</sub>	-	10.72	1000
GdMgAl <sub>11</sub> O <sub>19</sub>	-	10.63	1000
LaTi <sub>2</sub> Al <sub>9</sub> O <sub>19</sub> (LTA)	1.0-1.3	8.0-11.2 (200-1400°C)	300-1500
RE <sub>3</sub> TaO <sub>7</sub> (RE=La, Nd, Sm, Eu, Gd, Dy)	1.1-2.1	-	25-900
RE <sub>3</sub> NbO <sub>7</sub> (RE=Dy, Y, Er, Yb)	1.25-1.55	-	1000
RETaO <sub>4</sub> (RE=Nd, Eu, Gd, Dy, Er, Yb, Lu)	1.38-1.94	-	800
Lu <sub>3</sub> TaO <sub>7</sub>	-	10.72	1200
RENbO <sub>4</sub> (RE=Nd, Sm, Gd, Dy, Er, and Yb)	1.80-2.26	9.8-11.6	1000
Dy <sub>3</sub> NbO <sub>7</sub>	-	11.0	1200
(La <sub>0.2</sub> Nd <sub>0.2</sub> Sm <sub>0.2</sub> Eu <sub>0.2</sub> Gd <sub>0.2</sub> ) <sub>2</sub> Ce <sub>2</sub> O <sub>7</sub>	0.92	~12.0	1400
(La <sub>0.2</sub> Nd <sub>0.2</sub> Sm <sub>0.2</sub> Gd <sub>0.2</sub> Yb <sub>0.2</sub> ) <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>	0.9	10.9	1000
(La <sub>0.2</sub> Ce <sub>0.2</sub> Nd <sub>0.2</sub> Sm <sub>0.2</sub> Eu <sub>0.2</sub> ) <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>	0.76	-	-
(5RE <sub>1/5</sub> ) <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>	< 1	-	300-1200
RETa <sub>3</sub> O <sub>9</sub>	1.5-2.0	8.0-10.1 (at 1200°C)	25-900
(Sm <sub>0.2</sub> Eu <sub>0.2</sub> Tb <sub>0.2</sub> Dy <sub>0.2</sub> Lu <sub>0.2</sub> ) <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>	0.86	11.0	1000

### **3.1. Yttria Stabilized Zirconia (YSZ)**

The  $Y_2O_3 \cdot ZrO_2$  (YSZ) system is one of the materials that most fully satisfies the requirements for ceramic coatings, the composition of which is optimized according to the criterion of maximum durability and corresponds to the content of 6-8 wt%  $Y_2O_3$  [13]. YSZ has such desirable properties as high fracture toughness ( $\sim 3 \text{ MPa}\cdot\text{m}^{1/2}$ ), high CTE ( $\sim 11 \times 10^{-6} \text{ K}^{-1}$ ), low thermal conductivity ( $\sim 2.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at  $1000^\circ\text{C}$ ), low Young's modulus ( $\sim 240 \text{ GPa}$ ), high melting point ( $\sim 2700^\circ\text{C}$ ), relatively low density ( $\sim 6.4 \text{ g}\cdot\text{cm}^{-3}$ ), high hardness ( $\sim 14 \text{ GPa}$ ) and good stability [1-3,11,15,16]. Unfortunately, the practical application of YSZ is seriously restricted due to its inherent phase transformation and enhanced (accelerated) sintering. At temperatures beyond  $1200^\circ\text{C}$ , YSZ changes its crystal structure from a metastable tetragonal phase to tetragonal and cubic phase and then, during cooling, the tetragonal phase transforms into a monoclinic phase [4,15]. The phase transformation always leads to a strong change in the volume (3-5%) of the material, which is accompanied by the formation of cracks in the coating and ultimately leads to delamination and destruction of the TBC [5]. A large number of researchers have studied how to modify YSZ using a variety of techniques, such as adding other rare-earth elements as stabilizers of zirconia, doping and co-doping with various rare-earth elements, preparing gradient coating materials and so on, to improve YSZ's thermophysical properties further, prevent its phase transition and increase the operating temperature. However, it is still difficult to improve YSZ and increase its application temperature, which limits its further application at ultra-high temperatures. Therefore, it is very important to develop a new type of ceramic material – alternatives to YSZ – for advanced applications of TBC with better phase stability and lower thermal conductivity at higher temperatures to further increase the temperature at the GTE inlet.

### **3.2. Alternative Ceramic Materials**

In recent decades, research efforts have focused on the development and production of ceramic TBCs for gas turbine parts, as traditional turbine materials have reached thermal limits. Various approaches are being explored to create reliable and robust TBCs to replace conventional YSZ coatings [5-7,12,16,22-24,30,35,37]. However, there is still no material that can completely replace YSZ like TBC ceramic, because it has a ferroelastic hardening effect, which greatly increases its strength and facilitates its application in harsh environments. Ceramic materials matching all the requirements are still very rare in terms of the current standard. Therefore, low thermal conductivity (below  $2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ) and appropriate CTE (above  $10 \times 10^{-6}\cdot\text{K}^{-1}$ ) are considered to be the main selection criteria for ceramic materials for TBC applications. Recently, the search for research has expanded and the study and application of pyrochlore, perovskites, hexaaluminate, rare-earth tantalates/niobates and high-entropy oxides have begun [17-21,30]. Some of them have found application as an outer layer or as stabilized oxides of TBC in aero GTEs.

#### **3.2.1. Pyrochlore oxides ( $A_2B_2O_7$ )**

Pyrochlore oxides ( $A_2B_2O_7$ ) are relatively new candidate materials suitable for TBC applications due to their superior phase stability and relatively lower thermal

conductivity than conventional YSZ. In this composition  $A_2B_2O_7$ , A usually represents rare-earth elements such as La to Lu, and B represents commonly transition elements such as Ti, Zr and Hf. Such great attention to pyrochlores is due to the close relationship of their structure with fluorites ( $ZrO_2$ ,  $CeO_2$ ,  $HfO_2$ ). The pyrochlore structure resembles that of fluorite (like the  $Y_2O_3$ - $ZrO_2$  system), but it has a lot more displaced oxygen atoms and one less oxygen atom than fluorite. If we consider the YSZ system as pyrochlore  $Y_2Zr_2O_7$ , it will be unstable with respect to the disordered fluorite material  $(ZrO_2)_2$ - $Y_2O_3$ , i.e. strongly doped YSZ. However, when the Y is replaced by larger rare-earth elements such as La or Gd, a stable pyrochlore structure is produced that can withstand temperatures of at least  $1500^\circ\text{C}$ . Similarly, when the Zr ion is substituted with a Ti or Mo, the pyrochlore structure is also stabilized [22].

In pyrochlores, various substitutions of elements at the A and B sites allow obtaining materials with low thermal conductivity for TBC applications [3]. Indeed, at temperatures between  $700^\circ\text{C}$  and  $1200^\circ\text{C}$ , pyrochlore compounds of rare-earth zirconates  $Re_2Zr_2O_7$  (such as  $La_2Zr_2O_7$ ,  $Eu_2Zr_2O_7$ ,  $Sm_2Zr_2O_7$ ,  $Nd_2Zr_2O_7$ , and  $Gd_2Zr_2O_7$ ) show extremely low thermal conductivity, ranging from  $\sim 1.1$ – $1.7 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  [22,23]. In addition, other pyrochlores such as  $La_2Hf_2O_7$ ,  $Pr_2Hf_2O_7$ ,  $Ce_2Zr_2O_7$ , and  $Sm_2Ti_2O_7$  also exhibit reduced thermal conductivity at elevated temperatures and remain phase stable all the way to their melting points [24]. The decrease was explained by the scattering of phonons by point defects.

Lanthanum zirconate  $La_2Zr_2O_7$  (or LZ) is one of the potential TBC materials that has been widely investigated due to its desirable characteristics, including a low thermal conductivity ( $1.56 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ), a high melting point ( $2700^\circ\text{C}$ ), better thermal stability up to the melting point, and lower sintering ability compared to YSZ [12]. However, the application of LZ is limited by its lower thermal cycle life compared to YSZ due to its low CTE ( $9.1 \times 10^{-6} \text{ K}^{-1}$ ) and fracture toughness ( $1.4 \text{ MPa}\cdot\text{m}^{1/2}$ ) [6,24]. Among the other rare-earth zirconates,  $Nd_2Zr_2O_7$  ( $9.6 \times 10^{-6} \text{ K}^{-1}$ ),  $Eu_2Zr_2O_7$  ( $9.5 \times 10^{-6} \text{ K}^{-1}$ ) and  $Gd_2Zr_2O_7$  ( $10.4 \times 10^{-6} \text{ K}^{-1}$ ) are also attractive candidates for TBC due to their high CTE values (greater than LZ), but unfortunately, their low lifetime also limits their application, as in the case of LZ [24].

Hence, in order to improve the fracture toughness, further reduce the thermal conductivity, and also enhance their CTE, doping and co-doping of pyrochlores with other rare-earths have been proposed. Both A and B sites can be replaced by a variety of other elements with similar ionic radii, as long as electrical neutrality is maintained. The doping element can create many point defects in the pyrochlore crystal structure, which can improve the scattering of phonons, resulting in a decrease in thermal conductivity and a slight increase in CTE [5,6,22,24].

Many studies have been carried out on the doping of pyrochlores in the direction of improving their thermal properties. Lehmann et al. studied LZ doping with Nd, Eu, and Gd, and in the case of doping with gadolinium, the thermal conductivity was reduced from  $\sim 1.55 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  to  $\sim 0.9 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  (up to  $800^\circ\text{C}$ ) and the CTE also improved and its value enhanced from  $\sim 8.4 \times 10^{-6} \text{ K}^{-1}$  to  $\sim 9.2 \times 10^{-6} \text{ K}^{-1}$  (at  $1200^\circ\text{C}$ ) [19,27]. Zhu et al. conducted similar studies of doping LZ with Yb and Gd, and  $La_{1.7}Gd_{0.15}Yb_{0.15}Zr_2O_7$  showed

the lowest thermal conductivity compared to un-doped LZ, and doped materials  $\text{La}_{1.7}\text{Gd}_{0.3}\text{Zr}_2\text{O}_7$  and  $\text{La}_{1.7}\text{Yb}_{0.3}\text{Zr}_2\text{O}_7$  [25]. Guo et al. investigated the doping of  $\text{Gd}_2\text{Zr}_2\text{O}_7$  with  $\text{Yb}_2\text{O}_3$ . The thermal conductivities of synthesized  $(\text{Gd}_{1-x}\text{Yb}_x)_2\text{Zr}_2\text{O}_7$  ( $x = 0, 0.1, 0.3, 0.5, 0.7$ ) ceramics is in the range of  $0.88\text{-}1.00 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at  $1400^\circ\text{C}$ , which is 20% lower than that of traditional  $\text{Gd}_2\text{Zr}_2\text{O}_7$  ( $\sim 1.18 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ), and  $(\text{Gd}_{0.9}\text{Yb}_{0.1})_2\text{Zr}_2\text{O}_7$  composition demonstrates the lowest thermal conductivity value. The values of CTEs of these ceramics were measured in the range of  $11.8\text{-}13.0 \times 10^{-6} \text{ K}^{-1}$  at  $1200^\circ\text{C}$ , which is higher than that of the YSZ [26]. Wan et al. proposed the partially replace or co-use of Zr with the Ti in  $\text{Gd}_2\text{Zr}_2\text{O}_7$ . Doping with Ti can improve the properties of  $\text{Gd}_2\text{Zr}_2\text{O}_7$ , while the thermal conductivity of sintered  $\text{Gd}_2(\text{Zr}_{1-x}\text{Ti}_x)_2\text{O}_7$  ( $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$ ) is greatly decreased, and the CTE slightly increased, and  $\text{Gd}_2(\text{Zr}_{0.8}\text{Ti}_{0.2})_2\text{O}_7$  showed a maximum value of  $\sim 11.8 \times 10^{-6} \text{ K}^{-1}$  (at  $1000^\circ\text{C}$ ) [27]. The LZ with  $\text{CeO}_2$  was investigated as TC material [28]. Sintered  $\text{La}_2(\text{Zr}_{0.5}\text{Ce}_{0.5})_2\text{O}_7$  and  $\text{La}_2(\text{Zr}_{0.7}\text{Ce}_{0.3})_2\text{O}_7$  demonstrated better characteristics than un-doped  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{La}_2\text{Ce}_2\text{O}_7$ . The fracture toughness of  $3.8 \pm 0.2 \text{ MPa}\cdot\text{m}^{1/2}$  and  $3.5 \pm 0.2 \text{ MPa}\cdot\text{m}^{1/2}$  (which is higher) and thermal conductivity of  $1.14 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  and  $1.06 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  (which is lower) [28]. Wang et al. chose La to dope the  $\text{Yb}_2\text{Sn}_2\text{O}_7$  ceramic based on the consideration that La and Yb ions have the largest radii difference in the lanthanide group, resulting in significant disorders. Among the obtained  $(\text{La}_x\text{Yb}_{1-x})_2\text{Sn}_2\text{O}_7$  ( $x=0.3,0.5,0.7$ ) compositions,  $(\text{La}_{0.5}\text{Yb}_{0.5})_2\text{Sn}_2\text{O}_7$  showed the lowest thermal conductivity ( $0.85 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at RT) and highest CTE ( $13.53 \times 10^{-6} \text{ K}^{-1}$  at  $950^\circ\text{C}$ ) [29]. According to the results of the study, doping and especially co-doping of pyrochlore oxides can significantly increase their properties.

Compared to conventional ceramic materials, coatings using  $\text{A}_2\text{B}_2\text{O}_7$  type compounds have very outstanding features, including lower thermal conductivity, higher thermal stability, and higher CTE. The thermodynamic properties of materials have been improved to varying degrees by doping with different elements, whether single-element or multi-element. However, there are some drawbacks as well, such as an inappropriate CTE (higher than 8YSZ but still lower than the BC) and low-value fracture toughness.

### **3.2.2. Perovskite oxides ( $\text{ABO}_3$ )**

The perovskites ( $\text{ABO}_3$ ) have been suggested as potential materials for TBC applications due to their refractory qualities. In the general formula of perovskite, A is a rare-earth or alkaline earth metal, and B is a general transition metal [5]. The perovskites have a number of properties, including a high melting point (above  $2000^\circ\text{C}$ ), low thermal conductivity (below  $2.2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ), and relatively high CTE (above  $8.5\text{-}9.0 \times 10^{-6} \text{ K}^{-1}$ ), making them suitable for TBC applications [5,6,15]. Only a few perovskite materials have been studied as candidates for TBCs, such as  $\text{SrZrO}_3$  and  $\text{BaZrO}_3$ . Initially,  $\text{BaZrO}_3$  was thought of as a possible contender for the use of TBC, which can be explained by its high melting point of  $2600^\circ\text{C}$ . However, further studies have shown that a number of shortcomings, such as relatively low CTE, poor chemical stability, and relatively high thermal conductivity, lead to the destruction of the coating and deprive it of being a candidate for TC materials [30]. While  $\text{SrZrO}_3$  proved to be a suitable candidate for TC and has attracted more attention due to its features such as high melting point ( $2650^\circ\text{C}$ ), thermal conductivity close to YSZ ( $2.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ), good chemical compatibility, and



relatively high CTE ( $10.8 \times 10^{-6} \text{ K}^{-1}$ ) [5,31,32]. In addition, perovskites can also substitute elements at sites A and/or B, which allows selective influence on the material's properties. This, in turn makes it possible to obtain new complex perovskites, such as  $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$  (BMT) and  $\text{La}(\text{Al}_{1/4}\text{Mg}_{1/2}\text{Ta}_{1/4})\text{O}_3$  (LAMT). BMT has the highest melting point ( $\sim 3000^\circ\text{C}$ ) and is considered one of the most refractory oxides, and its thermal conductivity is  $2.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at  $1100^\circ\text{C}$ . LAMT has a low thermal conductivity of about  $2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  and a high CTE of approximately  $11.9 \times 10^{-6} \text{ K}^{-1}$  [5,23]. However, although they have such good properties, the applications of BMT and LAMT are limited due to their disadvantages such as low strength and poor thermal shock resistance, which shorten the thermal cycle life. It should also be noted that complex perovskite compounds decompose during the deposition process, which is accompanied by the formation of a second phase. The aforementioned  $\text{SrZrO}_3$ , despite its good thermal properties, has disadvantages such as low fracture toughness. Moreover,  $\text{SrZrO}_3$  has polymorphism and inevitably undergoes phase transformation accompanied by volume change. For example, at about  $740^\circ\text{C}$ ,  $\text{SrZrO}_3$  undergoes a transition from orthorhombic to pseudo-tetragonal phase with a volume change of  $\sim 0.14\%$  [31,32]. Many researchers have considered various ways to improve the performance of  $\text{SrZrO}_3$  for use as a promising TBC material. For instance, Ma et al. investigated the improvement of  $\text{SrZrO}_3$ 's properties by doping with rare-earth metals and chose  $\text{YbO}_2$  and  $\text{GdO}_2$  as dopants at a molar ratio of 10% and 20%, respectively [33]. Thus,  $\text{Sr}(\text{Zr}_{0.9}\text{Yb}_{0.1})\text{O}_{2.95}$  and  $\text{Sr}(\text{Zr}_{0.8}\text{Gd}_{0.2})\text{O}_{2.9}$  ceramic materials were synthesized, and then their effect on the properties of  $\text{SrZrO}_3$  was investigated. According to the results of the study, doping with  $\text{GdO}_2$  can improve the phase stability of  $\text{SrZrO}_3$  and prevent its phase transition, while doping with  $\text{YbO}_2$  shifted the phase transition temperature of  $\text{SrZrO}_3$  to low values (from  $\sim 740^\circ\text{C}$  to  $\sim 630^\circ\text{C}$ ). Thermal conductivity tests show that both dopants can improve the thermal conductivity of  $\text{SrZrO}_3$ , but doping with  $\text{Yb}_2\text{O}_3$  rather than  $\text{Gd}_2\text{O}_3$  reduces its thermal conductivity more effectively.  $\text{Sr}(\text{Zr}_{0.9}\text{Yb}_{0.1})\text{O}_{2.95}$  demonstrated  $\sim 20\%$  lower thermal conductivity over the entire temperature range under study compared to undoped  $\text{SrZrO}_3$ . Therefore, doping not only suppresses the phase transition but also reduces the thermal conductivity of perovskites, and makes  $\text{Sr}(\text{Zr}_{0.9}\text{Yb}_{0.1})\text{O}_{2.95}$  and  $\text{Sr}(\text{Zr}_{0.8}\text{Gd}_{0.2})\text{O}_{2.9}$  potential candidates for TC.

Strontium cerate ( $\text{SrCeO}_3$ ) is another new perovskite candidate material that has been suggested by Yuan et al. [34].  $\text{SrCeO}_3$  demonstrated a low thermal conductivity of  $1.74\text{-}2.84 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  (RT- $800^\circ\text{C}$ ) and at  $200\text{-}1300^\circ\text{C}$  the CTE was  $9.67\text{-}10.6 \times 10^{-6} \text{ K}^{-1}$ . Compared to the traditional YSZ, it is relatively high. Also,  $\text{SrCeO}_3$  exhibits superior phase stability without phase transitions up to  $1300^\circ\text{C}$ . Due to the aforementioned properties,  $\text{SrCeO}_3$  can become a potential candidate for TC at temperatures above  $1200^\circ\text{C}$ , but at the same time, it has such disadvantages as low fracture toughness ( $1.09 \text{ MPa}\cdot\text{m}^{1/2}$ ), low sintering resistance, and composition deviation, which lead to early coating failure and limit its further application.

Shishkin [35] investigated the improvement of the properties of the  $\text{SrCeO}_3$  material due to the substitution of cerium and choose Sn as a dopant. Sn was selected from a range of materials based on a previous study [36], where La, Pr, Y, and Sn were selected for light doping of strontium cerate. The reason why Sn was chosen is described by such aspects as the difference between the electronegativity of Sn and Ce as well as atomic radii, Sn's

chemical compatibility with Ce, and the relatively inexpensive initial SnO<sub>2</sub> precursors. All this makes Sn a good dopant material for improving the properties of SrCeO<sub>3</sub>. The great difference in the atomic radii between Ce (0.87Å) and Sn (0.69Å) leads to substantial distortions of the crystal lattice, which, in turn, affects the decrease in thermal conductivity and its values decrease from 1.9 W·m<sup>-1</sup>·K<sup>-1</sup> to 1.4 W·m<sup>-1</sup>·K<sup>-1</sup> at 1000°C with increasing tin content. An increase in CTE is also observed, up to x≤0.3 the CTE values continue to increase, and SrCe<sub>0.7</sub>Sn<sub>0.3</sub>O<sub>3</sub> showed a maximum value of 12.47×10<sup>-6</sup> K<sup>-1</sup> (1100°C), but at x>0.3, the CTE values begin to decrease slightly and the smallest value is 12.26×10<sup>-6</sup> K<sup>-1</sup> (at x=0.5), which is still greater than YSZ. According to the results, among the synthesized SrCe<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub> (x=0.1...0.5) ceramics, the SrCe<sub>0.5</sub>Sn<sub>0.5</sub>O<sub>3</sub> has the most stable composition and showed the finest combination of low thermal conductivity and high CTE value, which makes it a promising material for use as TC.

### **3.2.3. Lanthanide hexaaluminates (AB<sub>x</sub>Al<sub>12-x</sub>O<sub>19</sub>)**

Lanthanide hexaaluminate LnMAl<sub>11</sub>O<sub>19</sub> oxides with a magnetoplumbite-like structure have been found to be a prospective material for TC applications, due to their excellent properties, such as high CTE, high melting point, high stress tolerance, low thermal conductivity, and lower sintering ability. In this composition LnMAl<sub>11</sub>O<sub>19</sub>, Ln is a usually rare-earth metal La to Gd, and M is a divalent metal, such as Mg, Mn to Co. These oxides have a plate-like structure with a well-balanced micro porosity, which makes it possible to obtain coatings with low thermal conductivity. Among these oxides, the most attractive and studied material is LaMgAl<sub>11</sub>O<sub>19</sub> (or LaMA) due to its thermo-physical and mechanical properties that are comparable to or better than those of YSZ. LaMA has a low thermal conductivity (1.95 W·m<sup>-1</sup>·K<sup>-1</sup>), a relatively high CTE (10.95×10<sup>-6</sup> K<sup>-1</sup>), a low Young's modulus, a high melting point, a high degree of sintering resistance, and structural and thermal stability up to 1600°C [37,38]. Also, there are other rare-earth aluminates, such as PrMgAl<sub>11</sub>O<sub>19</sub>, NdMgAl<sub>11</sub>O<sub>19</sub>, SmMgAl<sub>11</sub>O<sub>19</sub>, EuMgAl<sub>11</sub>O<sub>19</sub>, and GdMgAl<sub>11</sub>O<sub>19</sub>, which have been investigated by Haoran et al. [38]. LnMgAl<sub>11</sub>O<sub>19</sub> (where Ln is Pr, Nd, Sm, Eu, and Gd) ceramics demonstrate lower thermal conductivities compared to YSZ. At 20–1000°C, the thermal conductivity of GdMgAl<sub>11</sub>O<sub>19</sub> was 1.79–2.05 W·m<sup>-1</sup>·K<sup>-1</sup>. The CTE at 1000°C for PrMgAl<sub>11</sub>O<sub>19</sub>, NdMgAl<sub>11</sub>O<sub>19</sub>, SmMgAl<sub>11</sub>O<sub>19</sub>, EuMgAl<sub>11</sub>O<sub>19</sub>, and GdMgAl<sub>11</sub>O<sub>19</sub> are 10.91×10<sup>-6</sup> K<sup>-1</sup>, 10.86×10<sup>-6</sup> K<sup>-1</sup>, 10.79×10<sup>-6</sup> K<sup>-1</sup>, 10.72×10<sup>-6</sup> K<sup>-1</sup>, 10.63×10<sup>-6</sup> K<sup>-1</sup>, respectively, which are lower compared to LaMgAl<sub>11</sub>O<sub>19</sub>, but the smallest value is still higher than that of YSZ at 1000°C. LaTi<sub>2</sub>Al<sub>9</sub>O<sub>19</sub> (LTA), a different hexaaluminate, was suggested and researched as a potential TBC material by Xie et al. [39]. LTA exhibits a low thermal conductivity of 1.0-1.3 W·m<sup>-1</sup>·K<sup>-1</sup> (300–1500°C) and a relatively high CTE of 8.0-11.2×10<sup>-6</sup> K<sup>-1</sup> (200-1400°C), which are comparable to YSZ. Moreover, LTA shows superior phase stability up to 1600°C. However, LTA has a low fracture toughness (0.9-1.7MPa·m<sup>1/2</sup>), which reduces its service life and limit its application. Despite the shortcomings of LTA, its advantages make it a potential candidate for TBC at 1300°C.

Lanthanide hexaaluminates have attractive qualities, such as a low thermal conductivity, a high CTE, high melting point, low sinterability, and exhibit structural stability at elevated temperatures. Also, as in the case of other oxides, doping of these compositions makes it possible to improve their properties (i.e., reduce thermal conductivity, increase CTE, etc.).

But in general, oxides of this type have not been widely studied compared to the previous types of oxides, so there is a need for extensive study of these materials to propose a new material for TC applications that can replace traditional YSZ.

### **3.2.4. Rare-earth tantalates and niobates**

Another promising alternative material appropriate for TC is rare-earth tantalates and niobates. In recent years, rare-earth tantalates and niobates have attracted more attention, due to their interesting properties [4,40-43,46]. The rare earth tantalates and niobates have a high melting point (above 2000°C), extremely low thermal conductivity ( $\sim 1-2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ), relatively high CTE ( $\sim 10-11 \times 10^{-6} \text{ K}^{-1}$ ), superior phase stability (up to 1500°C) and outstanding mechanical properties. The rare-earth tantalates and niobates have two main crystal structures: pyrochlore with a defective fluorite structure  $\text{RE}_3\text{BO}_7$  and perovskite structure  $\text{REBO}_4$  (where B=Ta, Nb) [4].

The  $\text{RE}_3\text{BO}_7$  and  $\text{REBO}_4$  compounds exhibit lower thermal conductivities than that of YSZ. Indeed,  $\text{RE}_3\text{TaO}_7$  (RE=La, Nd, Sm, Eu, Gd, Dy) have a thermal conductivity of  $1.1-2.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  (25–900°C) [40], and  $\text{RE}_3\text{NbO}_7$  (RE=Dy, Y, Er, Yb) –  $1.25-1.55 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at 1000°C [4]. Also,  $\text{RETaO}_4$  (RE=Nd, Eu, Gd, Dy, Er, Yb, Lu) shows thermal conductivity of 1.38 to  $1.94 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at 800°C [41], and  $\text{RENbO}_4$  (RE=Nd, Sm, Gd, Dy, Er, and Yb) –  $1.80-2.26 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at 1000°C [4]. The  $\text{RE}_3\text{BO}_7$  and  $\text{REBO}_4$  ceramics show relatively high CTE.  $\text{RE}_3\text{NbO}_7$  (RE = La, Nd, Sm, Eu, Gd, Dy) was investigated as a TC candidate. As a result, CTE increased with decreasing  $\text{RE}^{3+}$  ionic radius, and  $\text{Dy}_3\text{NbO}_7$  exhibited the highest value of  $11.0 \times 10^{-6} \text{ K}^{-1}$  at 1200°C [42]. Also according to other research the CTE of  $\text{RENbO}_4$  (RE = Y, La, Nd, Sm, Gd, Dy, Yb) ceramics are in the range of  $9.8-11.6 \times 10^{-6} \text{ K}^{-1}$  [43], and  $\text{Lu}_3\text{TaO}_7$  –  $10.72 \times 10^{-6} \text{ K}^{-1}$  at 1200°C [44], which are comparable to other TC materials. It should also be noted that  $\text{REBO}_4$  demonstrates high fracture toughness. For instance,  $\text{RENbO}_4$  (RE = Nd, Sm, Gd, Dy, Er, and Yb) have a fracture toughness that falls between  $1.93-2.77 \text{ MPa}\cdot\text{m}^{1/2}$ . Such values are related to the ferroelastic structure of these materials, as in the case of YSZ. Although these values are relatively lower than YSZ, they are still higher than most other materials [45]. Unfortunately,  $\text{RE}_3\text{BO}_7$  displays lower fracture toughness values than  $\text{REBO}_4$ , but is comparable to rare-zirconates, which is their disadvantage. For example, the fracture toughness of  $\text{RE}_3\text{NbO}_7$  (RE = La, Nd, Sm, Eu, Gd) is in the range of  $0.5-1.6 \text{ MPa}\cdot\text{m}^{1/2}$  [46].

### **3.2.5. High-entropy ceramics (HECs)**

High-entropy ceramics (HECs) are a new family of single-phase ceramics that contain multi-principal components in which five or more different elements in an equimolar or near-equimolar ratio simultaneously occupy one or more Wyckoff positions. This type of oxide was first proposed as  $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$  in 2015 by Rost et al [47]. HEC has brought a new concept to the ceramics world and thereby changed the early understanding of ceramic materials and still continues to attract more and more attention. HECs have gained more interest because of some appealing features, such as low thermal conductivity, relatively high CTE, slow (sluggish) grain growth rate, chemical and structural stability, improved wear, corrosion and oxidation resistance, increased hardness and toughness, and enhanced phase stability at high temperatures [48,49]. The

reason why HECs have amazing properties compared to single-component ceramics is due to the synergistic effect of multi-component elements. The essence of this effect is that the atoms of different elements in multicomponent HEC randomly occupy cationic positions, which causes significant differences in atomic mass, ionic radius, and interatomic strength, and leads to a highly disordered and distorted crystal structure [1,50]. This, in turn, greatly enhances phonon scattering, and makes it possible to obtain materials with low thermal conductivity, as well as improved properties.

A high-entropy material  $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})_2\text{Ce}_2\text{O}_7$  with a fluorite structure was designed by Xue et al [1]. The synthesized material demonstrates a low thermal conductivity ( $0.92 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ) and high CTE ( $\sim 12.0 \times 10^{-6} \text{ K}^{-1}$ ) at  $1400^\circ\text{C}$ . Moreover  $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})_2\text{Ce}_2\text{O}_7$  exhibits superior phase stability up to  $1400^\circ\text{C}$ . Liu et al. synthesized high-entropy rare-earth zirconate  $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$  with fluorite structure and investigated its properties [49].  $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$  showed superior thermophysical properties, such as low thermal conductivity of  $0.9 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  and relatively high CTE of  $10.9 \times 10^{-6} \text{ K}^{-1}$  (at  $1000^\circ\text{C}$ ), and excellent mechanical properties, such as large Young's modulus (257 GPa) and high fracture toughness ( $2.7 \text{ MPa}\cdot\text{m}^{1/2}$ ), as well as good phase stability up to  $1200^\circ\text{C}$ . New HEC material  $(\text{La}_{0.2}\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{Zr}_2\text{O}_7$ , which has very low thermal conductivity ( $0.76 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ) from others was prepared by Zhao et al. [51]. The thermal conductivity and other properties of high-entropy rare-earth zirconates  $(5\text{RE}_{1/5})_2\text{Zr}_2\text{O}_7$  were investigated at  $300\text{--}1200^\circ\text{C}$ . The thermal conductivity is  $< 1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ . It also exhibits improved sintering resistance and outstanding thermal stability [52]. The properties of other high-entropy perovskite  $\text{RETa}_3\text{O}_9$  ceramics have been investigated [48]. These ceramics have lower thermal conductivity of  $1.5\text{--}2.0 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at  $25\text{--}900^\circ\text{C}$ , relatively high CTE of  $8.0\text{--}10.1 \times 10^{-6} \text{ K}^{-1}$  (at  $1200^\circ\text{C}$ ), moderate Young's modulus (140–180GPa) and increased fracture toughness ( $1.8\text{--}2.5 \text{ MPa}\cdot\text{m}^{1/2}$ ). Ren et al. [50] prepared high-entropy rare-earth zirconate  $(\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2}\text{Lu}_{0.2})_2\text{Zr}_2\text{O}_7$  with a defective fluorite structure, and reported that the synthesized zirconate has an ultra-low thermal conductivity of  $0.86 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  and greater CTE of about  $11 \times 10^{-6} \text{ K}^{-1}$  at  $1000^\circ\text{C}$ , as well as high Young's modulus (257GPa) and fracture toughness ( $2.24 \text{ MPa}\cdot\text{m}^{1/2}$ ), and also demonstrate high-temperature phase stability up to  $1400^\circ\text{C}$ . HECs show better performance than their single component compounds. In general, the performance of HECs can be described by four features: high entropy, severe lattice distortion, sluggish diffusion, and cocktail effect, due to which they demonstrate excellent thermophysical and mechanical properties [49,52].

#### **4. RESULTS**

Although a complete description of all possible materials for TBCs is of great interest, their engine applications and those of primary interest have been studied in this paper. Among the properties listed above, the CTE and thermal conductivity are the most important properties for selecting materials for the TC layer of TBC. When considering the choice of TC material, if the required temperature will be below  $1200^\circ\text{C}$ , then YSZ based material is still the best choice due to its overall properties. However, in our case, this selected TC material to be used in a TBC system will be applied to parts operating at high

temperatures. Currently, new ceramic candidates (such as pyrochlore, perovskites, high-entropy oxides and other structures) are increasingly being studied to replace the existing YSZ, with the aim of developing TBCs with higher temperature capability, lower thermal conductivity and longer lifetime. Perovskite type oxides often appear to have rather low thermal and chemical stability, although the physical properties are quite encouraging. The properties of perovskites can be further improved by doping. However, there are still disadvantages, such as low toughness and phase instability, that significantly limit its use. In some cases, several of the pyrochlores have good physical properties and sufficient stability. The rare-earth tantalates and niobates exhibit outstanding thermo-mechanical properties and are potential candidates for TC applications. It is especially worth noting that REBO<sub>4</sub> ceramics show better properties and are more promising due to their ferroelasticity, which makes them a real contender for TBC.

There are many oxide materials that meet the intended requirements and are considered suitable for use as a ceramic TC layer in the TBC system. One of them and the most promising candidate is pyrochlore type oxide - Lanthanum zirconate (La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, LZ), which is characterized by low thermal conductivity and very high thermal stability compared to other traditional TBC systems. Compared with YSZ, LZ has several advantages for TBC applications. This includes the absence of phase transformation from room temperature to its melting temperature, significantly high sintering resistance, better CMAS resistance, a very low thermal conductivity and lower oxygen ion diffusivity, which protects the BC layer and the substrate from oxidation. However, the thermal cycling performance of this oxide is excellent (when applied over YSZ as a two-layer system or using graded coatings with YSZ). The main disadvantage of LZ is its low CTE, which can be overcome by doping some elements into LZ.

In many cases, the performance of this oxide material depends on its compatibility with the BC and substrate materials (i.e., their properties are close to each other), the construction of the TBC system, and the correct selection of the application method.

## **5. CONCLUSIONS**

This paper describes the characteristics, advantages and disadvantages of TC materials in recent years, and summarizes the directions of research and development of alloying modification of traditional ZrO<sub>2</sub>-based materials and new ceramic materials. According to the results of the analysis, it was determined that the composition, production technology and structure of TC materials directly affect the structure of coatings and their future properties. Compared with YSZ ceramic oxides, pyrochlore, perovskites, lanthanide hexaaluminates, rare-earth tantalates and niobates, and other new ceramic materials have better thermal insulation resistance, high temperature oxidation resistance, high-temperature phase stability and other properties. However, thermal expansion coefficient mismatch and insufficient fracture toughness problems still limit the application of these listed new materials.

Pyrochlore type oxides are considered the most potential TC material with superior thermal and mechanical performance. TC should be considered as a complex coating system rather than as an individual coating layer or addition to the substrate. In other

words, the component must be designed as an integral part of the assembly. The compatibility of the coating on other layers of TBC with each other, that is, the compatibility of material properties, is a factor that directly affects the overall property of TBC. Along with the correct selection of the coating composition in the layers, attention should also be paid to other factors, including the correct choice of TBC construction, coating thicknesses, application methods and process parameters, etc.

## REFERENCES

- [1] Y. Xue, X. Zhao, Y. An, Y. Wang, M. Gao, H. Zhou, J. Chena, *High-entropy (La<sub>0.2</sub>Nd<sub>0.2</sub>Sm<sub>0.2</sub>Eu<sub>0.2</sub>Gd<sub>0.2</sub>)<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub>: A potential thermal barrier material with improved thermo-physical properties*, Journal of Advanced Ceramics **11**(4), 615–628 (2022).
- [2] D.R. Clarke, M. Oechsner, N.P. Padture, *Thermal barrier coatings for more efficient gas-turbine engines*, MRS Bulletin **37**(10), 891-898 (2012).
- [3] N.P. Padture, M. Gell, E.H. Jordan, *Thermal barrier coatings for gas-turbine engine applications*, Science **296**, 280–284 (2002).
- [4] Z.Y. Wei, G.H. Meng, L. Chen et al., *Progress in ceramic materials and structure design toward advanced thermal barrier coatings*, Journal of Advanced Ceramics **11**(7), 985–1068 (2022).
- [5] A. Pakseresht, F. Sharifianjazi, A. Esmaeilkhanian, L. Bazli, M.R. Nafchi, M. Bazli, K. Kirubaharan, *Failure mechanisms and structure tailoring of YSZ and new candidates for thermal barrier coatings: A systematic review*, Materials and Design **222**, 111044 (2022).
- [6] S. Wu, Y. Zhao, W. Li, W. Liu, Y. Wu, F. Liu, *Research Progresses on Ceramic Materials of Thermal Barrier Coatings on Gas Turbine*, Coatings **11**(1), 79 (2021).
- [7] J. Song, L. Wang, J. Yao, H. Dong, *Multi-Scale Structural Design and Advanced Materials for Thermal Barrier Coatings with High Thermal Insulation: A Review*, Coatings **13**, 343 (2023).
- [8] A.G. Evans, D.R. Mumm, J.W. Hutchinson, G.H. Meier, F.S. Pettit, *Mechanisms controlling the durability of thermal barrier coatings*, Progress in Materials Science **46**(5), 505–553 (2001).
- [9] R. Sivakumar, B.L. Mordike, *High temperature coatings for gas turbine blades: A review*, Surface and Coatings Technology **37**(2), 139-160 (1989).
- [10] A.M. Karlsson, J.W. Hutchinson, A.G. Evans, *The displacement of the thermally grown oxide in thermal barrier systems upon temperature cycling*, Materials Science and Engineering A **351**, 244-257 (2003).
- [11] K. Kokini, Y.R. Takeuchi, B.D. Choules, *Surface thermal cracking of thermal barrier coatings owing to stress relaxation: zirconia vs mullite*, Surface and Coatings Technology **82**, 77-82 (1996).
- [12] X.Q. Cao, R. Vassen, D. Stoeber, *Ceramic materials for thermal barrier coatings*, Journal of the European Ceramic Society **24**(1), 1–10 (2004).
- [13] R. Vaßen, E. Bakan, D.E. Mack, O. Guillon, *Perspective on Thermally Sprayed Thermal Barrier Coatings: Current Status and Trends*, Journal of Thermal Spray Technology **31**(4), 685–698 (2022).

- [14] S. Stecura, *Effects of Compositional Changes on the Performance of a Thermal Barrier Coating System*, Washington: NASA TM-78976, National Aeronautics and Space Administration, 1978.
- [15] E. Bakan, R. Vaßen, *Ceramic Top Coats of Plasma-Sprayed Thermal Barrier Coatings: Materials, Processes, and Properties*, Journal of Thermal Spray Technology **26**, 992–1010 (2017).
- [16] H.F. Chen, C. Zhang, Y.C. Liu, P. Song, W.-X. Li, G. Yang, B. Liu, *Recent progress in thermal/environmental barrier coatings and their corrosion resistance*, Rare Metals **39**(8), 498-512 (2020).
- [17] D. Zhu, R.A. Miller, *Thermal Conductivity and Sintering Behavior of Advanced Thermal Barrier Coatings*, Ceramic Engineering and Science Proceedings **23**(4), 457–468 (2002).
- [18] M. Maloney, US Patents. 6 177 200 and 6 231 991, 2001.
- [19] H. Lehmann, D. Pitzer, G. Pracht, R. Vassen, D. Stöver, *Thermal conductivity and thermal expansion coefficients of the lanthanum rare-earth-element zirconate system*, Journal of the American Ceramic Society **86**(8), 1338-1344 (2003).
- [20] N.P. Padture, P.G. Klemens, *Low Thermal Conductivity in Garnets*, Journal of the American Ceramic Society **80**(4), 1018-1020 (1997).
- [21] O. Sudre, J. Cheung, D. Marshall, P. Morgan, C.G. Levi, "Thermal Insulation Coatings of LaPO<sub>4</sub>", in the *25th Annual International Conference on Composites, Advanced Ceramics, Materials and Structures: B, Cocoa Beach of Florida, Westerville, OH, USA, January 2001*, Mrityunjay Singh and Todd Jessen. American Ceramic Society, 2001, pp. 367–74.
- [22] D.R. Clarke, S.R. Phillpot, *Thermal Barrier Coating Materials*, Materials today **8**(6), 22–29 (2005).
- [23] W. Pan, S.R. Phillpot, C. Wan, A. Chernatynskiy, Z. Qu, *Low Thermal Conductivity Oxides*, MRS Bulletin **37**(10), 917– 922 (2012).
- [24] X.Q. Cao, *Application of Rare-Earths in Thermal Barrier Coating Materials*, Journal of Materials Science Technology **23**(1), 15-35 (2007).
- [25] D. Zhu, D.S. Fox, N.P. Bansal, and R.A. Miller, *Advanced Oxide Material Systems for 1650 °C Thermal and Environmental Barrier Coating Applications*, Washington: NASA/TM-2004–213219, National Aeronautics and Space Administration, 2004.
- [26] L. Guo, H. Guo, H. Peng, S. Gong, *Thermophysical properties of Yb<sub>2</sub>O<sub>3</sub> doped Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and thermal cycling durability of (Gd<sub>0.9</sub>Yb<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>/YSZ thermal barrier coatings*, Journal of the European Ceramic Society **34**(5), 1255–1263 (2014).
- [27] C. Wan, Z. Qu, A. Du, W. Pan, *Influence of B Site Substituent Ti on the Structure and Thermophysical Properties of A<sub>2</sub>B<sub>2</sub>O<sub>7</sub>-Type Pyrochlore Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>*, Acta Materialia **57**(16), 4782-4789 (2009).
- [28] W. Ma, X. Li, Y. Yin, H. Dong, Y. Bai, J. Liu, D. Nan, J. Wang, *The mechanical and thermophysical properties of La<sub>2</sub>(Zr<sub>1-x</sub>Ce<sub>x</sub>)<sub>2</sub>O<sub>7</sub> ceramics*, Journal of Alloys and Compounds **660**, 85-92 (2016).
- [29] J. Wang, F. Xu, R.J. Wheatley, K. Choy, N.C. Neate, X. Hou, *Investigation of La<sup>3+</sup> Doped Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> as new thermal barrier materials*, Materials & Design **85**, 423–430 (2015).
- [30] R. Vaßen, X. Cao, F. Tietz, D. Basu, D. Stöver, *Zirconates as new materials for thermal*

- barrier coatings*, Journal of the American Ceramic Society **83**, 2023-2028 (2004).
- [31] W. Ma, D. Mack, R. Vaßen, D. Stöver, *Perovskite-Type Strontium Zirconate as a New Material for Thermal Barrier Coatings*, Journal of the American Ceramic Society **91**(8) 2630–2635 (2008).
- [32] W. Ma, M.O. Jarligo, D.E. Mack, D. Pitzer, J. Malzbender, R. Vaßen, D. Stöver, *New Generation Perovskite Thermal Barrier Coating Materials*, Journal of the Thermal Spray Technology **17**(5), 831-837 (2008).
- [33] W. Ma, D. Mack, J. Malzbender, R. Vaßen, D. Stöver, *Yb<sub>2</sub>O<sub>3</sub> and Gd<sub>2</sub>O<sub>3</sub> doped strontium zirconate for thermal barrier coatings*, Journal of the European Ceramic Society **28**(16), 3071–3081 (2008).
- [34] J. Yuan, J. Sun, J. Wang, H. Zhang, S. Dong, J. Jiang, L. Deng, X. Zhou, X. Cao, *SrCeO<sub>3</sub> as a novel thermal barrier coating candidate for high-temperature applications*, Journal of Alloys and Compounds **740**, 519–528 (2018).
- [35] R.A. Shishkin, *Structure and thermal properties of SrCe<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub> (x=0.1...0.5) as a promising thermal barrier coating*, Ceramics International **49**(19), 31539-31548 (2023).
- [36] R.A. Shishkin, O.G. Reznitskikh, A.Yu. Suntsov, V.L. Kozhevnikov, *Properties of SrCe<sub>0.95</sub>Mo<sub>0.05</sub>O<sub>3</sub> (M = La, Pr, Y, Sn) thermal barrier materials*, Ceramics International **48**(18), 27003-27010 (2022).
- [37] H. Zeya, L. Haoran, W. Chang-An, *Synthesis and characterization of LaMgAl<sub>11</sub>O<sub>19</sub> as thermal barrier coatings material*, Key Engineering Materials **697**, 390–394 (2016).
- [38] L. Haoran, W. Chang-An, Z. Chenguang, T. Shuyan, *Thermo-physical properties of rare-earth hexaaluminates LnMgAl<sub>11</sub>O<sub>19</sub> (Ln: La, Pr, Nd, Sm, Eu and Gd) magnetoplumbite for advanced thermal barrier coatings*, Journal of the European Ceramic Society **35**(4), 1297–1306 (2015).
- [39] X. Xie, H. Guo, S. Gong, H. Xu, *Lanthanum-Titanium-Aluminum Oxide: A Novel Thermal Barrier Coating Material for Applications at 1300°C*, Journal of the European Ceramic Society **31**(9), 1677-1683 (2011).
- [40] L. Chen, J. Feng, *Research progress of thermomechanical properties of rare-earth tantalates RE<sub>3</sub>TaO<sub>7</sub> and RETa<sub>3</sub>O<sub>9</sub> ceramics*, Advanced Ceramics. **40**(6), 367–397 (2019).
- [41] J. Wang, X.Y. Chong, R. Zhou, J. Feng, *Microstructure and thermal properties of RETaO<sub>4</sub> (RE = Nd, Eu, Gd, Dy, Er, Yb, Lu) as promising thermal barrier coating materials*, Scripta Materialia **126**, 24–28 (2017).
- [42] L. Chen, P. Wu, P. Song, J. Feng, *Potential thermal barrier coating materials: RE<sub>3</sub>NbO<sub>7</sub> (RE = La, Nd, Sm, Eu, Gd, Dy) ceramics*, Journal of the American Ceramic Society **101**(10), 4503–4508 (2018).
- [43] F. Wu, P. Wu, Y. Zhou, X. Chong, J. Feng, *The thermo-mechanical properties and ferroelastic phase transition of RENbO<sub>4</sub> (RE = Y, La, Nd, Sm, Gd, Dy, Yb) ceramics*, Journal of the American Ceramic Society **103**(4), 2727–2740 (2019).
- [44] W. Sang, H. Zhang, H.-h. Chen, Y. Guo, J. Ling, X.-g. Chen, W. Xie, *Preparation and thermophysical properties of Lu<sub>3</sub>TaO<sub>7</sub>*, Ceramics International **48**(11), 15848-15854 (2022).
- [45] P. Zhang, Y. Feng, Y. Li, W. Pan, P.-an Zong, M. Huang, Y. Han, Z. Yang, H. Chen, Q.



- Gong, Ch. Wan, *Thermal and mechanical properties of ferroelastic  $RENbO_4$  ( $RE = Nd, Sm, Gd, Dy, Er, Yb$ ) for thermal barrier coatings*, Scripta Materialia **180**, 51–56 (2020).
- [46] L. Chen, J. Guo, Y. Zhu, M. Hu, J. Feng, *Features of crystal structures and thermo-mechanical properties of weberites  $RE_3NbO_7$  ( $RE = La, Nd, Sm, Eu, Gd$ ) ceramics*, Journal of the American Ceramic Society **104**(1), 404–412 (2020).
- [47] C.M. Rost, E. Sacht, T. Borman, A. Moballegh, E.C. Dickey, D. Hou, J.L. Jones, S. Curtarolo, J.-P. Maria, *Entropy-stabilized oxides*, Nature Communications **6**, 8485 (2015).
- [48] L. Chen, B. Li, J. Guo, Y. Zhu, J. Feng, *High-entropy perovskite  $RETa_3O_9$  ceramics for high-temperature environmental/thermal barrier coatings*, Journal of Advanced Ceramics **11**, 556–569 (2022).
- [49] D. Liu, B. Shi, L. Geng, Y. Wang, B. Xu, Y. Chen, *High-entropy rare-earth zirconate ceramics with low thermal conductivity for advanced thermal-barrier coatings*, Journal of Advanced Ceramics **11**, 961–973 (2022).
- [50] K. Ren, Q. Wang, G. Shao, X. Zhao, Y. Wang, *Multicomponent high-entropy zirconates with comprehensive properties for advanced thermal barrier coating*, Scripta Materialia **178**, 382–386 (2020).
- [51] Z. Zhao, H. Xiang, F.Z. Dai, Z. Peng, Y. Zhou,  *$(La_{0.2}Ce_{0.2}Nd_{0.2}Sm_{0.2}Eu_{0.2})_2Zr_2O_7$ : A novel high-entropy ceramic with low thermal conductivity and sluggish grain growth rate*, Journal of Materials Science & Technology **35**(11), 2647–2651 (2019).
- [52] F. Li, L. Zhou, J.X. Liu, Y. Liang, G.-J. Zhang, *High-entropy pyrochlores with low thermal conductivity for thermal barrier coating materials*, Journal of Advanced Ceramics **8**, 576–582 (2019).

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