Ultralow Thermal Conductivity in Highly Anion-Defective Aluminates

Chunlei Wan, Zhixue Qu, Yong He, Dong Luan, and Wei Pan*

State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing, 100084, China

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Ultralow thermal conductivity ($1.1\ \mathrm{W/m\cdot K}$, $1000\ ^\circ\mathrm{C}$) in anion-deficient Ba_2RAlO_5 ($R =$ Dy, Er, Yb) compounds was reported. The low thermal conductivity was then analyzed by kinetic theory. The highly defective structure of Ba_2RAlO_5 results in weak atomic bond strength and low sound speeds, and phonon scattering by large concentration of oxygen vacancies reduces the phonon mean free path to the order of interatomic distance. Ba_2DyAlO_5 exhibits the shortest phonon mean free path and lowest thermal conductivity among the three compositions investigated, which can be attributed to additional phonon scattering by DyO_6 octahedron tilting as a result of a low tolerance factor. The Ba_2RAlO_5 ($R =$ Dy, Er, Yb) compounds have shown great potential in high-temperature thermal insulation applications, particularly as a thermal barrier coating material.

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Materials with low thermal conductivity have been of increasing interest in the thermal insulation part of high-temperature engines ranging from gas turbines to power generation and diesels [1]. A reduced thermal conductivity of thermal insulation materials enables those engines to work at higher temperature with a consequent improvement of thermal efficiency. Up until now much effort, including both theory and experiment, has been made in search of low thermal conductive materials. Clarke raised a general guideline describing structure features of prospective low thermal conductive materials as high average atomic weight, loose bonding, and highly disordered and distorted structures [2,3]. Thermal conductivities of many materials have been examined for potential thermal barrier coatings (TBC) application [4–6]. One of the most successful is the discovery of 7 wt % yttria stabilized zirconia (7YSZ), which has already become a commonly used TBCs composition today. Thermal conductivity of YSZ, as low as $2.5\ \mathrm{W/(m\cdot K)}$ at $1000\ ^\circ\mathrm{C}$, is almost temperature independent from room temperature to high temperature, which has originally been attributed to the presence of high concentration of oxygen vacancies [7]. Another advance is the pyrochlore-type rare-earth zirconate, with one eighth of the oxygen atoms missing, which even achieve thermal conductivity as low as $1.5\ \mathrm{W/(m\cdot K)}$ at $1000\ ^\circ\mathrm{C}$ [8–10]. Both cases support the significance of oxygen vacancies in obtaining low thermal conductivity, as oxygen vacancy scatters phonons in virtue of both missing atom and missing interatomic linkages [7].

In this Letter, we studied thermal conductivity of Ba_2RAlO_5 ($R =$ Dy, Er, Yb), according to the fact that it has even higher oxygen vacancies than previous materials. Ba_2RAlO_5, which is a variant of perovskite structure, has attracted little attention since its discovery in the 1980s [11]. It is monoclinic with space group $P2_1/m$ or $P2_1$. All Ba_2RAlO_5 compounds have a distinct pseudo-b.c.c. subcell, which shows similarity with the perovskite structure (ABO_3). The transformation matrix from true cell of perovskite to Ba_2RAlO_5 is

$$\begin{pmatrix} \bar{1} & \bar{1} & \bar{1} \\ 1 & \bar{1} & 1 \\ \bar{1} & 0 & 1 \end{pmatrix}.$$

The Ba atom in Ba_2RAlO_5 corresponds to the "*A*" atom in perovskite and *R* and Al occupy the site of the "*B*" atom. One sixth of the oxygen atoms are missing in Ba_2RAlO_5, making this structure highly defective. X-ray diffraction (XRD) results also reveal the existence of the superstructure, which suggests an ordered arrangement of *R* and Al atoms as well as oxygen vacancies in this compound.

Ba_2RAlO_5 samples were synthesized by the solid state reaction method. $BaCO_3$, R_2O_3, and Al_2O_3 powders were weighted and mixed in appropriate ratio. The mixture was then placed in an alumina crucible and calcined at 1200 °C for 8 h. The resultant powder was then sieved (200 mesh) and hot-press sintered at 1500 °C for 4 h under the pressure of 25 MPa to prepare bulk materials for properties measurement. For comparison, $Gd_2Zr_2O_7$ was also synthesized using the solid state reaction method and densified through hot-press sintering.

The phase composition was examined by x-ray diffraction. The density (ρ) was measured using the Archimedes technique and the relative density of all the Ba_2RAlO_5 and $Gd_2Zr_2O_7$ samples were all above 96%. Thermal diffusivity (α) was obtained using a laser flash analyzer (Netzsch LFA 427, Germany) [12] and the error of measurement is within ±2% [13]. Heat capacity (C_p) was calculated from the literature values [14] of its constituent oxides (BaO, R_2O_3, Al_2O_3) by Neumann-Kopp rule, which has been verified to give a value within ±3% of the experimental one [9]. Thermal conductivity (k') was then obtained using the relation

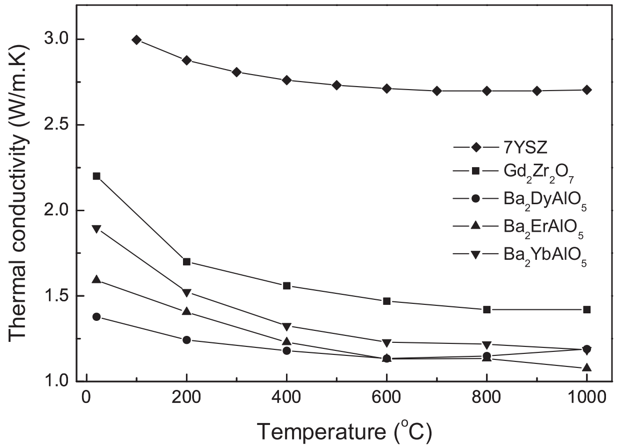

FIG. 1. Thermal conductivities of Ba_2RAlO_5 ($R =$ Dy, Er, Yb), $Gd_2Zr_2O_7$ and 7YSZ 3. The error bars were omitted, since the standard deviation was smaller than the symbol size.

$$k' = \alpha C_p \rho. \tag{1}$$

Combining the results of thermal diffusivity and heat capacity, the overall error of thermal conductivity is estimated to be less than ±5%. In order to remove the effect of porosity and attain a reasonable comparison with other materials, the thermal conductivity values were extrapolated to the 100% dense case (k) by calibration relation [15]:

$$k'/k = 1 - 4/3\phi, \tag{2}$$

where Φ is the porosity. The elastic constants were derived from the longitudinal and transverse acoustic speeds which were measured with an ultrasonic pulser and receiver (Panametrics 5900PR, US) [16]. The thermal expansion coefficient was analyzed by a high-temperature dilatometer (Netzsch DIL 402EP, Germany).

Thermal conductivities of Ba_2RAlO_5 compounds and $Gd_2Zr_2O_7$ are shown in Fig. 1 and the value of 7YSZ [3], the state-of-art materials of TBCs, are also included for comparison. It can be noticed that thermal conductivities of Ba_2RAlO_5 have achieved $1.1\ \mathrm{W/m \cdot K}$ at 1000 °C and smaller than half of that of 7YSZ and 20% lower than that of $Gd_2Zr_2O_7$. It is almost the lowest value that can ever be obtained for those refractory oxides which can be stable above 1500 °C [5].

In order to understand the low thermal conductivity of Ba_2RAlO_5, we refer to Debye's phonon gas theory, in which thermal conduction process was considered as energy exchange between phonons [17]:

$$k' = 1/3 C_V l v. \tag{3}$$

Where C_v is the heat capacity per unit volume, l is the phonon mean free path and v is the sound speed. C_v makes limited contribution to high-temperature thermal conductivity, according to the fact that the value of C_v approaches $3k_B$ per atom at temperatures in excess of Debye temperature, as predicted by the Dulong-Petit equation. Therefore, low thermal conductivity mainly comes from short mean free path and low sound speed. Phonon mean free path is associated with phonon scattering processes in this compound and sound speed is determined by atomic bond strength and density.

Sound speed including both longitudinal (ν_P) and transverse (ν_S) speeds has been measured by ultrasonic reflection method. Average sound speed was obtained by integration of these two speeds [2]:

$$\nu = 3^{1/3}\left(\frac{1}{\nu_P^3} + \frac{2}{\nu_S^3}\right)^{-1/3}. \tag{4}$$

The results are shown in Table I. and the values of 7YSZ and $Gd_2Zr_2O_7$ are also included. It can be noticed that the Ba_2RAlO_5 compounds have smaller sound speed than 7YSZ and $Gd_2Zr_2O_7$. Low sound speed seems to be a key factor of low thermal conductivity, as in D. G. Gahill's study [18], thermal conductivity of different materials has a strong dependence with their sound speeds. Sound speeds are mainly associated with atomic bond strength, which can be scaled by Young's modulus. In Table I, Young's moduli have been obtained by sound speeds. Ba_2RAlO_5 compounds exhibit much lower Young's modulus than others, which should arise from their highly defective structure. In addition, low Young's modulus is strongly favored for a TBC material, as it increase elastic compliance of the coating so as to enhance the thermal cycling stability of the whole TBC system [1].

Phonon mean free path can be calculated by combining Eq. (1) and (3),

$$l = 3\alpha/\nu. \tag{5}$$

Phonon mean free path of Ba_2RAlO_5 ($R =$ Dy, Er, Yb) as a function of temperature were plotted in Fig. 2. It can be noticed that the phonon mean free path of these compounds are all nearly within their lattice parameters ($a = 7.239$ Å, $b = 7.449$ Å, $c = 6.035$ Å for Ba_2DyAlO_5) [11] and at higher temperature, the phonon mean free

TABLE I. Sound speeds and Young's modulus of Ba_2RAlO_5 ($R =$ Dy, Er, Yb); published values of 7YSZ and $Gd_2Zr_2O_7$ are also included.

Composition	7YSZ	$Gd_2Zr_2O_7$	Ba_2DyAlO_5	Ba_2ErAlO_5	Ba_2YbAlO_5
Sound speed (m/s)	4326 [18]	3832 [19]	3078	2908	2901
Young's modulus (GPa)	250.0 [9]	234.3 [19]	116.5	100.3	109.4

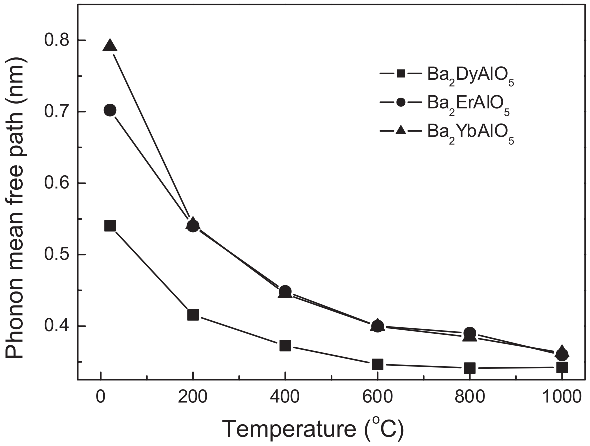

FIG. 2. Calculated phonon mean free path of Ba_2RAlO_5 ($R =$ Dy, Er, Yb).

path of all the compositions reaches a limit around 0.35 nm. There is an amorphous limit of thermal conductivity of solids, when phonons are completely uncoupled and energy is transferred between neighboring atoms. For this limit, the phonon mean free path achieves its minimum value which equals to the interatomic distance [2,18]. The interatomic distance can be estimated as the cube root of the volume of an atom. For Ba_2RAlO_5, the minimum phonon mean free path has been calculated to be 0.24, 0.24, and 0.23 nm, respectively. It can be noticed that real values of the phonon mean free path of Ba_2RAlO_5 have closely approached their amorphous limit, indicating a strong phonon scattering process inside.

For an electrical insulating material, scattering processes that can restrict the phonon mean free path involve phonon-phonon scattering, defect scattering, and boundary scattering [17]. In the present case, the magnitude of the phonon mean free path (~nm) is far smaller than that of the grain size (~μm), so boundary scattering can be ignored. For Ba_2RAlO_5 compounds, defect scattering (scattering by oxygen vacancy) should be a key factor that reduces their phonon mean free path to the order of interatomic distance. Oxygen vacancy scatters phonons in virtue of both missing mass and missing linkage and it has been identified as the major source of phonon scattering in stabilized zirconia [7], as well as rare-earth zirconate [9]. In Ba_2RAlO_5 compounds, one sixth of the oxygen atoms are missing, making the concentration of oxygen vacancy higher than the previous materials. Therefore, more phonon scattering resources can be expected, leading to a shorter phonon mean free path. In our previous work, the phonon mean free path of $Gd_2Zr_2O_7$ was determined to be 0.38 nm [19], which is a little higher than the values of Ba_2RAlO_5 compounds.

From Fig. 2, it can also be noticed that the phonon mean free path of Ba_2DyAlO_5 is comparatively lower than those of Ba_2ErAlO_5 and Ba_2YbAlO_5, except the limit case at 1000 °C. Since all the three compositions contain the same concentration of oxygen vacancies, there must be an additional phonon scattering mechanism in Ba_2DyAlO_5 that accounts for its relatively shorter mean free path. As has been known, Ba_2RAlO_5 compounds are all variant of perovskite (ABO_3), so their structure stability can be described by the tolerance factor [20]:

$$t = \frac{(r_{Ba} + r_O)}{\sqrt{2}(\bar{r}_{(R,\mathrm{Al})} + r_O)}, \tag{6}$$

where r_{Ba} is the radius of Ba^{2+}, r_O is radius of O^{2-}, and $\bar{r}_{(R,\mathrm{Al})}$ is the average radius of R^{3+} and Al^{3+}. Because of lanthanide contraction, Dy^{3+} has a larger radius than Er^{3+} and Yb^{3+}, so Ba_2DyAlO_5 has a smaller tolerance factor than the other two compositions. For monoclinic perovskite, which Ba_2RAlO_5 compounds belong to, a decrease of tolerance factor means that the BO_6 octahedron must be tilted so as to be matched with the AO_{12} polyhedron [20]. So in Ba_2DyAlO_5, BO_6 octahedron is most tilted, giving rise to additional phonon scattering compared with Ba_2ErAlO_5 and Ba_2YbAlO_5. Furthermore, the lowest phonon mean free path of Ba_2DyAlO_5 accounts for its lowest thermal conductivity, as shown in Fig. 1.

In fact, the increasing lattice instability with increase of the ion size of the rare-earth element in Ba_2RAlO_5 compounds can also be demonstrated by a rough estimation of melting point. We have prepared the Ba_2RAlO_5 compounds with most of the Lanthanide elements ($R =$ La, Nd, Sm, Gd, Dy, Er, Yb) and heated them to different temperatures (1500 °C, 1550 °C, 1600 °C, and 1650 °C). It turned out that Ba_2RAlO_5 ($R =$ La, Nd, Sm) melted below 1500 °C, Ba_2GdAlO_5 melted between 1500 °C and 1550 °C, and Ba_2RAlO_5 ($R =$ Dy, Er, Yb) did not melt until 1650 °C. This result also precludes use of those large-size elements of La, Nd, Sm, Gd from high-temperature applications in this Ba_2RAlO_5 compound.

Besides low thermal conductivity, the thermal expansion coefficient is also of particular interest for those high-temperature thermal insulation materials, since they are always in contact with other components in the system and thermal expansion compatibility between the different materials are required when temperature varies. For instance, in a thermal barrier coating system, the thermal expansion coefficient of the ceramic TBC material should be high enough to be matched with metallic bond coat (NiCrAlY, $13 \sim 17 \times 10^{-6}$ K^{-1}) [1,21]. In Fig. 3, thermal expansion coefficients of Ba_2RAlO_5 compounds are plotted as a function of temperature. It can be found that thermal expansion coefficients of the Ba_2RAlO_5 compounds approach $11.8–12.0 \times 10^{-6}$ K^{-1} at 1300 °C and exceed the corresponding values of 7YSZ (11.0×10^{-6} K^{-1}) and many other oxides that have been considered as potential TBC materials [5]. High thermal expansion coefficient of Ba_2RAlO_5 mainly comes from its highly defective structure, which leads to a low crystal energy. It can also be noticed that the value of Ba_2DyAlO_5 is higher than the other two compositions at high temperature, which

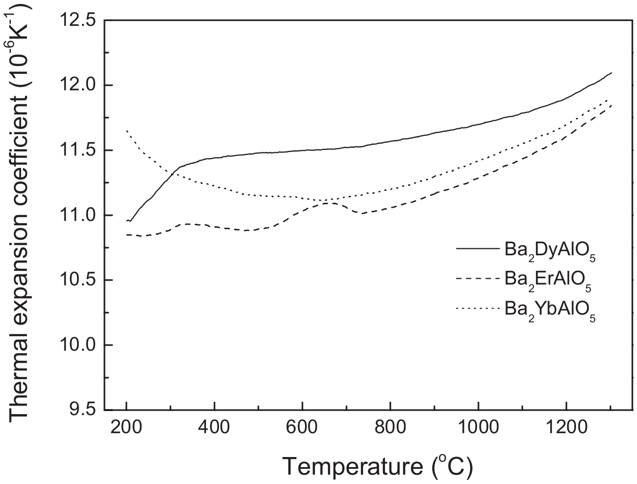

FIG. 3. Thermal expansion coefficients of Ba_2RAlO_5 ($R =$ Dy, Er, Yb).

possibly originates from its structure instability and DyO_6 octahedron tilting.

In summary, we reported ultralow thermal conductivity in anion-deficient Ba_2RAlO_5 ($R =$ Dy, Er, Yb) compounds. The low thermal conductivity was analyzed in terms of sound speed and phonon mean free path according to the kinetic theory. On one hand, large concentration of oxygen vacancies in Ba_2RAlO_5 compounds lead to low Young's modulus and consequent low sound speed, and on the other hand phonon scattering by oxygen vacancies reduces phonon mean free path to the order of interatomic distance. Ba_2DyAlO_5 exhibits shorter phonon mean free path and lower thermal conductivity than the other two compositions at lower temperature, which can be attributed to additional phonon scattering by RO_6 octahedron tilting as a result of its low tolerance factor. The low thermal conductive Ba_2RAlO_5 compounds have exhibited great potential in the high-temperature thermal insulation applications, particularly as a TBC material.

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*Corresponding author.
panw@mail.tsinghua.edu.cn

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[12] The measurement conforms to several international standards, including ASTM E 1461, DIN EN 821 and ISO 18755. Each specimen was machined into the shape of pellet (12.7 mm in diameter and 1 mm in thickness). Both sides of the specimen were coated with a thin layer of graphite and tested in flowing argon atmosphere. A laser pulse was used to heat one side of the specimen and the temperature rise of the opposite side was recorded using IR detector. Thermal diffusivity was then derived from the time dependence of the temperature rise through mathematical models [13]. Before test, pyrceram 9606, a standard thermal conductivity reference material, was used to calibrate the systematic error and the measured values were always within ±2% of literature values.

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