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New Oxide Compounds for Thermal Barrier Coating

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We report experimental thermal expansion coefficient and thermal conductivity of polycrystalline $Sr_2Nb_2O_7$ and La_2NiO_4. Hundreds of compounds are calculated from first principles using the full potential augmented plane wave method + local orbitals (APW+lo) and the full-potential local-orbital minimum-basis band-structure scheme (FPLO) using the coherent potential approximation (CPA). The thermal expansion coefficient (volume) α and the thermal conductivity λ are given as follows;

$\alpha(T) = \gamma(T)\, C_v(T) / (BV)$, $\lambda(T) = aB^{1.5} / (3\gamma(T)^2 \mathrm{sqrt}(\rho)\, T)$ (where T: absolute temperature, γ : average Grüneisen parameter, C_v: heat capacity, B: bulk modulus, V: molar volume, a: lattice constant, ρ :mean density). These compounds are compared with yttria-stabilized zirconia (YSZ), which is the conventional material for thermal barrier coating. For $Sr_2Nb_2O_7$, the thermal expansion coefficient (line) is 10×10^{-6}/K at 1273K and the thermal conductivity is 1.7W/(m · K). For La_2NiO_4, the thermal expansion coefficient is 14×10^{-6}/K and the thermal conductivity is almost same as that of YSZ.

In the melt-and-drip test, preferred oriented film of $Sr_2Nb_2O_7$ was obtained. By the improvement of production technique, it will be possible to produce preferred oriented film using cost effective thermal spraying.

Key words: thermal barrier coating, thermal expansion coefficient, thermal conductivity, first principle calculation

1. INTRODUCTION

The efficiency of gas turbine or jet engine is obviously improved by increasing the inlet gas temperature; so thermal barrier coatings (TBC) are widely used to protect thermally loaded components that are made of metal. Zirconia based material, for example yttria-stabilized zirconia (YSZ), is commonly used as conventional TBC material because of its high melting point, large thermal expansion coefficient and low thermal conductivity. Pure zirconia shows two reversible transformation; one is at around 1000℃, changing from the monoclinic form to the tetragonal form, and another is at 2370℃, changing from the tetragonal form to cubic form. It is impossible to use pure zirconia as structural material at high temperature because of the huge volume changing induced by that reversible transformation between the monoclinic form and the tetragonal form. Therefore, it is necessary to add some mol% of rare earths oxide like yttria to zirconia, to stabilize the tetragonal form, which is the phase of the temperature in use, at low temperature as well.

In this work, we tried to find some other new oxide compounds for TBC materials. The materials require large thermal expansion coefficient and low thermal conductivity for high resistance to failure. To find those new materials, we used the calculation technique. The candidates selected by calculations were prepared experimentally, and by measuring thermal expansion coefficient and thermal conductivity, it is clarified that calculation technique is quite efficient in finding some new compounds. Moreover, we tried to research the possibility of making preferred oriented films of these new oxide compounds by means of thermal spraying.

2. SCREENING METHOD

The most suitable material for TBC is searched by first principle calculations and databases. Hundreds of compounds are calculated from first principles using the full potential augmented plane wave method + local orbitals (APW+lo) in the generalized gradient approximation (GGA), and the full-potential local-orbital minimum-basis band-structure scheme (FPLO) using the coherent potential approximation (CPA) and Pseudo Potentials. The flow of screening system is shown in Fig. 1.

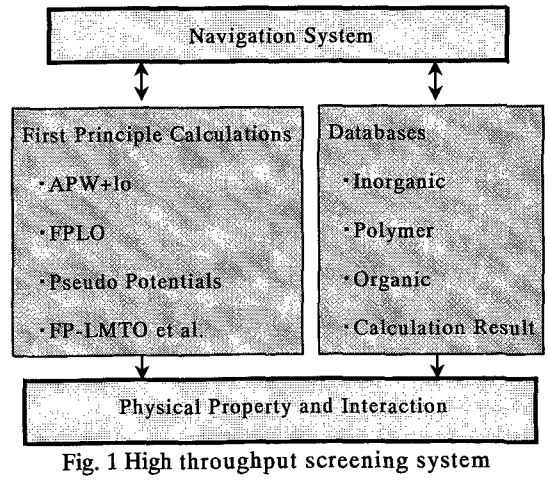

Fig. 1 High throughput screening system

The thermal expansion coefficient (volume) α and the thermal conductivity λ is as follows, respectively.

$$\alpha(T) = \gamma(T)\, C_v(T) / (B\, V) \quad \cdots (1)$$

$$\lambda(T) = (1/3)\, C\, v\, l \quad \cdots (2)$$

$$(\text{or} \quad \lambda(T) = a\, B^{1.5} / (3\, \gamma(T)^2 \,\text{sqrt}(\rho)\, T)) \quad \cdots (3)$$

where T: absolute temperature, γ: average Grüneisen parameter, C_v: heat capacity, B: bulk modulus, V: molar volume, a: lattice constant, ρ : mean density, C: specific heat per volume, v: velocity of phonon, l: mean free path of phonon.

For first screening, theoretical minimum value l_{min} was assumed [1] as follows.

$$\gamma(T) \fallingdotseq 2,\ C_v \fallingdotseq 3nR,\ l_{min} = v / f_{max} \quad (l_{min} \geqq a_{min}) \quad \cdots (4)$$

Where n: atoms in a unit cell, R: gas constant, f_{max}: highest phonon frequency, a_{min}: minimum lattice constant.

3. EXPERIMENTAL PROCEDURE

We found out some candidates from the calculation mentioned in the chapter 2. SCREENING METHOD, and tried to prepared specimens to measure their thermal expansion coefficient and thermal conductivity.

3.1 Specimen preparation

The specimens prepared are $Sr_3Ti_2O_7$, $Sr_2Nb_2O_7$, $LaTaO_4$, La_2NiO_4, $ZnTa_2O_6$, $Nd_3Ga_5O_{12}$, Mg_2SiO_4, Ni_2SiO_4, and $CaMgSiO_4$. All of these compounds were synthesized by conventional ceramic technique. Starting materials, which were powders of oxides or hydroxides, were mixed by ball milling for 16hrs. After drying out the mixed powders, they were calcined at 1400℃ for 2hrs. These calcined compounds were identified by XRD and found out to consist of a single phase.

3.2 Thermal expansion coefficient

The stick-like specimens (4×4×14mm) were cut out from the specimens sintered at 1500 ℃. Thermal expansion coefficient was measured from room temperature to 1400℃.

3.3 Thermal conductivity

The specimens of 1cm diameter and 1mm thickness were cut out from the specimens sintered at 1500℃. Thermal conductivity was measured by laser flash method.

3.4 Melt-and-drip test

The propose of this section is to show the possibility of making preferred oriented films using thermal spraying. The sintered specimen was melted in an infrared ray image furnace, and its melt was dripped on an $SrTiO_3$ substrate. The structure of oxide film obtained by melt-and-drip test was observed by SEM.

4. RESULTS AND DISCUSSION

4.1 Thermal expansion coefficient

Thermal expansion coefficient α is dependent on bulk modulus, which can be seen in the equation (1). If the bulk modulus is small, the material will be easily deformed. Then, searching the materials whose bulk modulus is small is one of the ways to find the materials of which thermal expansivity is large. We calculated the values of bulk modulus of $Sr_3Ti_2O_7$, $Sr_2Nb_2O_7$, $LaTaO_4$, La_2NiO_4, $ZnTa_2O_6$, $Nd_3Ga_5O_{12}$, Mg_2SiO_4, Ni_2SiO_4, $CaMgSiO_4$ and plotted them on the graph of Fig. 2. The experimental values are also shown in Fig. 2. The compounds whose bulk modulus is small tend to have relatively large thermal expansivity. Materials in dashed region seem to be promising.

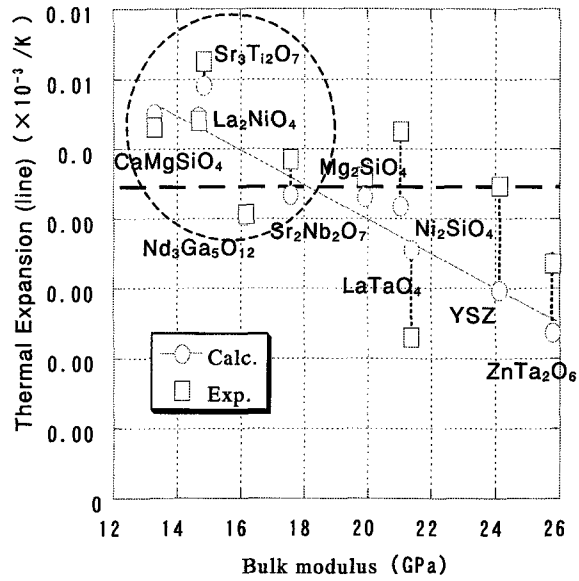

Fig. 2 The trend of thermal expansivity

4.2 Thermal conductivity

Minimum thermal conductivity is estimated from the equation (4). Though more accuracy will be required, materials in dashed region seem to be promising.

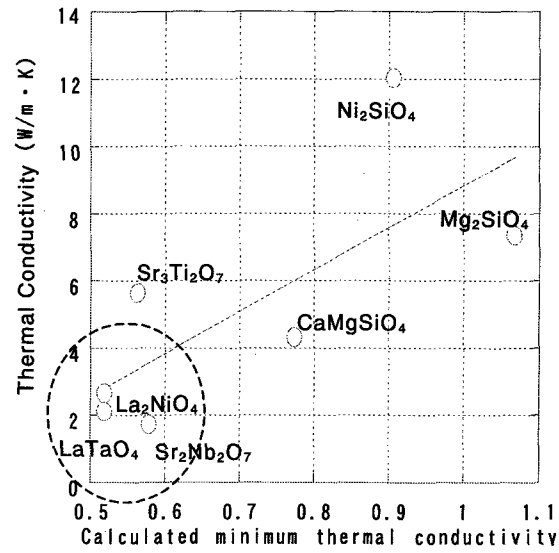

Fig. 3 Calculated minimum thermal conductivity and experimental values

4.3 Proposed compounds

Considering the results of 4.1 and 4.2, we can propose two compounds (and their similar compounds) as the new oxide compounds for TBC, because these compounds are better than YSZ in thermal properties as shown in Table 1.

Table 1 Thermal properties of proposed compounds

(at 1273K)	Present (YSZ)	$Sr_2Nb_2O_7$	La_2NiO_4
Thermal Conductivity	2.0 W(m·K)	1.7 W(m·K)	2.0 W(m·K)
Thermal Expansion	9.2×10^{-6}/K	10×10^{-6}/K	14×10^{-6}/K

The schematic images of the unit cell structure of $Sr_2Nb_2O_7$ and La_2NiO_4 are shown in Figs. 4-5. They seem to have weak intercalation bonds along b-axis, which may be the reason for large thermal expansivity.

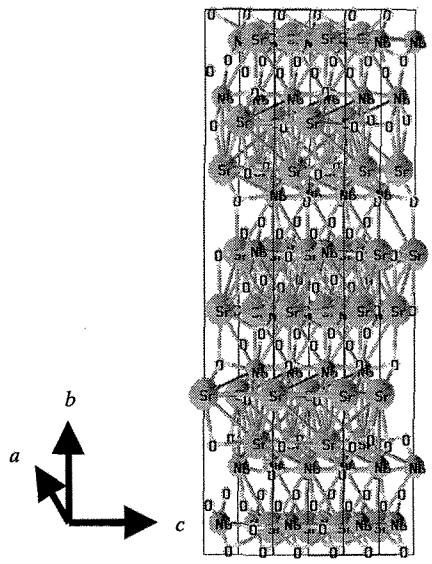

Fig. 4 Unit cell structure of $Sr_2Nb_2O_7$

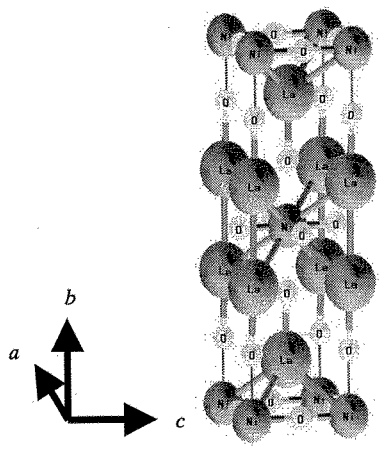

Fig. 5 Unit cell structure of La_2NiO_4

4.4 Melt-and-drip test

Model samples were made by the infrared ray image furnace. The scheme of infrared ray image furnace is shown in Fig. 6. Melted sample was dripped on an SrTiO3 substrate (a=0.3988nm). Fig. 7 shows XRD spectrum of dripped Sr2Nb2O7. The Strong (200) peak (d=0.1960nm) shows a-axis preferred orientation. Fig. 8 shows an SEM image of $Sr_2Nb_2O_7$ film. Perpendicular direction is the direction of thermal gradient. Columnar structure is observed because $Sr_2Nb_2O_7$ is an anisotropic plate-like crystal. This columnar structure may cause high resistance to failure. In addition, the film contains many pores; this may also have an effect on lowering thermal conductivity.

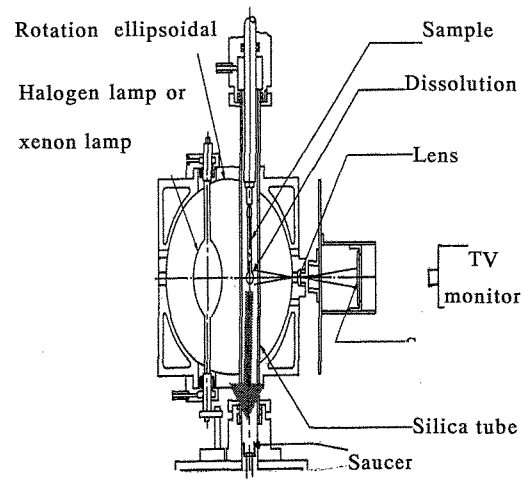

Fig. 6 Scheme of infrared ray image furnace

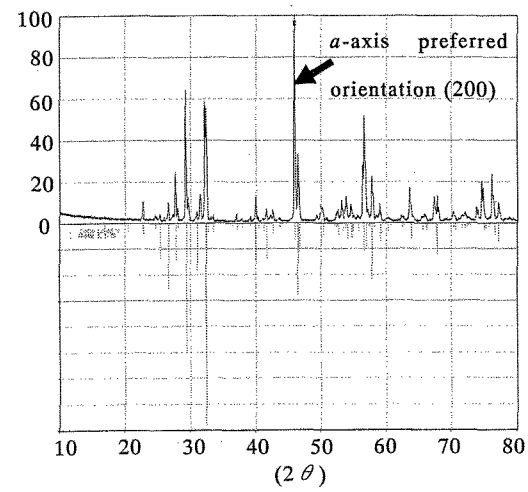

Fig. 7 XRD spectrum of dripped Sr2Nb2O7 (on SrTiO3 substrate a=0.3988nm)

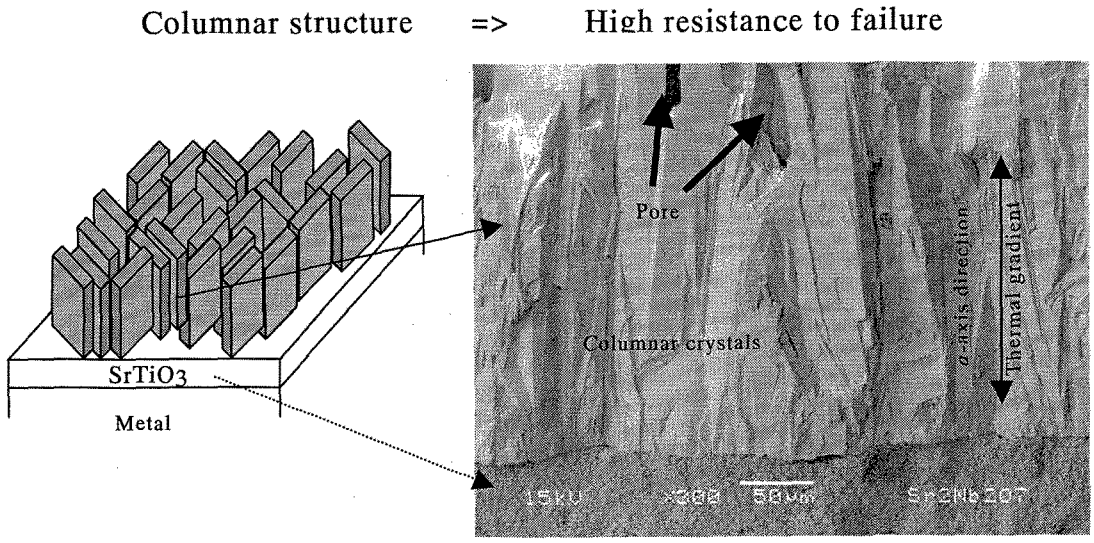

Fig. 8 SEM image of $Sr_2Nb_2O_7$ film
(on $SrTiO_3$ substrate a=0.3988nm)

5. CONCLUSION

We report experimental thermal expansion coefficient and thermal conductivity of polycrystalline $Sr_2Nb_2O_7$ and La_2NiO_4, which are searched by first principle calculations. These compounds are better than YSZ in thermal properties. These and their similar compounds are promising for TBC.

For $Sr_2Nb_2O_7$, the thermal expansion coefficient is 10×10^{-6}/K and thermal conductivity is 1.7W/(m・K) at 1273K. For La_2NiO_4, the thermal expansion coefficient is 14×10^{-6}/℃ and the thermal conductivity is almost same as that of YSZ.

By the melt-and-drip test, preferred oriented film of $Sr_2Nb_2O_7$ was obtained. It will be possible to produce preferred oriented film using thermal spraying by means of the improvement of production technique.

ACKNOWLEDGMENTS

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REFERENCES

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