Description for general public

The tailoring of insulating properties requires good understanding of the heat transfer phenomenon on the crystal structure level. In final product, e.g. plasma-sprayed ceramic layer, heat conductivity is a resultant of many factors, i.a. chemical composition, phase composition, rate of structural disorder, defects concentration and porosity. The idea of this project is to investigate ceramic materials in a way that would allow to separate different factors and provide knowledge regarding possible ways to improve thermal insulation properties of materials with ultra-low heat conductivity.

In ionic crystals, the heat is transferred mostly via so-called phonon mechanism, The increase in temperature causes the increase of energy of atoms' oscillation, which is passed to the adjacent atoms, and than to the next etc. Thus, when there is temperature gradient, the heat is transferred as a thermal wave propagating through the crystal. The quants of energy carried by this way are called phonons. Thus, in order to reduce heat transfer, the mobility of phonons needs to be obstructed. The first cause of phonon are anharmonic oscillations of crystal lattice. The former is responsible for the oscillation amplitude and the latter causes the displacement of equilibrium position. This effect is enhanced by the crystal structure defects, e.g. vacancies and foreign atoms, wherein those with high difference in atomic mass and ionic radius are the most efficient phonon scattering-centers.

The materials investigated in the research project are oxides with general formula $A_2B_2O_7$ and pyrochlore type of crystal lattice. The pyrochlore-type oxides, mostly $RE_2Zr_2O_7$ (RE – rare earth metals) are among the best ceramic thermal insulators due to their heavily defected structure – 1/8 oxygen sites are vacant in relation to the fluorite type oxides e.g. ZrO_2. The presence of large, heavy RE^{3+} ions and smaller, lighter Zr^{4+} ions is also conducive to lattice anharmonicity. However, the studies carried out in the recent years indicate that there is still potential to significantly decrease their heat conductivity, even by 20-30%.

The aim of the research project is the analysis of structural phenomena determining the possibilities of further reducing of heat conductivity in RE pyrochlores. The materials for the research will be synthesized via sol-gel type of method and sintered. The introduction of substitutional cations A' and B' in A and B sites, respectively, accordingly to the formula $(A_{1-x}A'_x)_2(B_{1-y}B'_y)_2O_7$ causes the mass fluctuation due to the mass difference and strain field fluctuation due to the ionic radii difference. Hence, the change in the crystal lattice dynamics, elastic properties and as a consequence, stronger phonon scattering should be expected. The next investigated effect will be compositionally-driven pyrochlore-defected fluorite phase transformation. The introduction of smaller substitutional cations in A site or bigger in B site in pyrochlores decrease the r_A/r_B ratio and drives the system towards the defected fluorite, increasing the rate of crystal lattice disorder. The influence of plane defects – crystallite boundaries and phase boundaries will be also taken into consideration in the research project.

The properly planned experiments will allow to distinguish the influence of various structural phenomena on the changes of heat conductivity. The evaluation of the impact of individual structural phenomena on the thermal properties (thermal diffusivity, specific heat, coefficient of thermal expansion) will allow to create semi-empirical model to predict the heat conductivity of pyrochlores as a function of the rate of substitution.

The research project presents the attempt to better understand the relation between structure and thermal properties and to approach the minimal values of thermal conductivity available for the defected ionic crystals. The pyrochlore-type oxides are perfect materials for this kind of study because they are very good thermal insulators and they are very susceptible to modification – there are thousands of possible combinations of chemical compositions and the changes in properties caused by substitutional cations may be radical.