

Short range investigation on $A_2Zr_2O_7$ with $A = Gd$ and Y synthesized by solid state reaction

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Abstract – Ionic conductivity has become a motivating field of technology since SOFCs were developed. $A_2B_2O_7$ pyrochlore structures are interesting atomic arrays having a structural hole that can facilitate conductivity by the jump of oxygen anions. On the other side, the Perturbed Angular Correlations (PAC) technique is one of the few techniques that can characterize atomic movements by measuring fluctuating electric field gradients due to charge movements within the order of nanoseconds. A PAC investigation on $Y_2Zr_2O_7$ and $Gd_2Zr_2O_7$ pyrochlores has been performed as a function of temperature. Results are compared together with those of $Pr_2Zr_2O_7$.

Stoichiometric solid solutions of several A_2O_3 and BO_2 oxides crystallizing in the pyrochlore structure $A_2B_2O_7$ are often used as electrolyte materials in solid oxide fuel cells. This application is related to the oxygen vacancies migration between specific oxygen sites [1,2]. Pyrochlores belong to the space group $Fd3m$ ($Z=8$) where the larger A^{3+} cations occupy the 16d sites, are eight coordinated and located within a distorted cubic polyhedron. The smaller B^{4+} cations are placed at 16c sites, six coordinated and located within a distorted octahedron. Six oxygen ions are at 48f positions and the seventh one is at 8a site, tetrahedrally coordinated to A cations. There exists an unoccupied interstitial site (8b) which is surrounded by four B ions.

It has been reported that cation disordering results in a transformation of the fully ordered pyrochlore structure into the defect-fluorite structure ($Fm3m$ with all A^{3+} , B^{4+} and O ions distributed randomly on the cation and oxygen fluorite sublattices), thus increasing the ionic conductivity [3]. At laboratory temperatures, a decrease of the cation ionic radius ratio $R = r_A/r_B$ below a critical value ($R_c = 1.44$) favors this situation [4]. In this work two pyrochlores of different R ratio have been investigated. The Perturbed Angular Correlation (PAC) Spectroscopy, a highly localized technique, is used to determine the electric field gradient at B sites in the $Y_2Zr_2O_7$ and $Gd_2Zr_2O_7$ compounds by exploiting the efficient PAC probes that constitute Hf natural impurities always existing in Zr. The aim has been to characterize the Zr^{4+} surroundings as a function of temperature focusing the attention on eventual thermal structure modifications and consequent changes in dynamical effects associated to ionic mobility. Results are compared with those reported for $Pr_2Zr_2O_7$.

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