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SEMI-EMPIRICAL PREDICTIONS FOR HARDNESS OF RARE EARTH PYROCHLORES; HIGH-PERMITTIVITY DIELECTRICS AND THERMAL BARRIER COATING MATERIALS[†]

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Herein, we have formulated a simplistic semi-empirical model for Vicker's hardness of rare earth based pyrochlore compounds. We have considered the $A_2^{+3}B_2^{+4}O_7$ structured 97 pyrochlore compounds for Vicker's hardness calculations. The plasmon energy ($\hbar\omega_p$) depends on basic parameters of the material such as N_e-effective number of free electrons per unit volume participating in plasma oscillations, *e*-electronic charge and *m*-mass of an electron. The proposed model predicts that the experimental and theoretical values of Vicker's hardness increases as plasmon energy of pyrochlore increases. We have found that the calculated values are in better agreement with available experimental and theoretical data, which supports the validity of the model. This model supports the modeling of emerging functional pyrochlore compounds and helps to understand their mechanical properties for excellent thermal stability, superconductivities, batteries, ferroelectricity, water spitting, high ionic conductivity, good photoluminescence, inherent oxygen vacancies, exotic magnetism, and now-a-days most importantly in nuclear waste encapsulation and aerospace industry.

Keywords: *Pyrochlores; Plasmon energy; Vicker's hardness*
PACS: 71.20.-b; 31.10. +Z; 81.05.Je; 61.50.-f; 81.70-q.

1. INTRODUCTION

Pyrochlore crystals have been a rapidly growing area of research for scientific community due to their unique technological applications such as exotic magnetism, low thermal conductivity (thermal barrier coatings on diesel engines), anti-erosion of Ag, nuclear waste management, catalysis, sensors, oxide fuel cell, lasers, and in various electronic devices due to unique crystal structure; and the broad range of the study of physical, electronic, mechanical, optical and thermal properties [1-4]. Oxides with Pyrochlore structure having rare earth (A) elements with the common formula ($A_2^{+3}B_2^{+4}O_7$) (A^{3+} = La^{3+}, Ce^{3+} , Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+} and Y^{3+} and B^{4+} = Sn^{4+}, Ti^{4+}, Zr^{4+}, Hf^{4+}, Ru^{4+}, Ir^{4+}etc), possess a different kind of the real-world uses since they have great melting points, large thermal expansion coefficient, high structural stability and low thermal conductivity [5-9]. Their complicated chemical structures make them susceptible to being quickly accommodated faults [10]. Pyrochlores are therefore a very promising candidate for usage as high-permittivity dielectrics [7], thermal barrier coatings (TBCs), solid-state electrolytes [12], nuclear wastage hosts [13] and catalysis [14]. Due to the numerous features of pyrochlores, research is being done to maximize the effectiveness of each attribute while maintaining the chemical and physical durability as well as the thermal consistency of pyrochlores. Liu et al. [13] carefully investigated $La_2R_2O_7$ (R = Ge, Ti, Sn, Zr, Hf) pyrochlores and noticed less heat conduction. It is too revealed why the La-O weak bonds affect the thermal and mechanical characteristics of these $La_2R_2O_7$ pyrochlores. Using density functional theory, the electronic structure, thermal and mechanical properties of Th-doped $Gd_2Zr_2O_7$ compounds studied by Zhao et al [15]. Feng et al. [4] predicted the elastic properties of rare earth stannate pyrochlores through density functional theory and ultrasonic resonance method.

Rare earth (Stannate, Titanate, Zirconate, Germenate and Hafnate) pyrochlore solids are of the molecular formula $A_2^{3+}B_2^{4+}O_7$, here A & B are metallic cations these can be either divalent and pentavalent or trivalent and tetravalent, respectively [16]. Rare earth pyrochlores ($A_2^{+3}B_2^{+4}O_7$) display cubic symmetry, space group *Fd-3m*, No. (227) with eight formula units per unit cell, wherein one-eighth of the anions are vacant to ensure charge neutrality and the cations form a face-centered cubic (FCC) array [17]. A-type cations occupy the *16d* (0.5, 0.5, 0.5) sites and the tetravalent atom B-type of cations occupy the *16c* (0, 0, 0) sites. Oxygen atom is situated at two locations: *O1* is located on the *8b* (0.375, 0.375, 0.375) site and *O2* on the *48f* (x, 0.125, 0.125) site [18] respectively. Lattice of atoms is completely explained in terms of structure parameter *x* defining the position of O (48f) atoms and the lattice size *a*. The *x* parameter determines the equilibrium position of O (48f) when, $0.3125 \leq x \geq 0.375$, and affects the local coordination around the A^{3+} and

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B^{4+}cations [17]. In the ideal pyrochlore structure with x = 0.3125 A-atoms and the B-atoms are coordinated at distorted cubes and regular octahedral, respectively. As the value of x approaches 0.375, the polyhedral at B site transform into tetragonal anti-prisms, while polyhedral of the rare earth elements at A-site become ordinary cubes. This arrangement of atoms is stable when, $1.46 \leq r_A/r_B \geq 1.78$ (r_A and $r_B$denote the radii of A^{3+} and B^{4+}cations, respectively) [19], while $(r_A/r_B) < 1.46$ results in a stable fluorite structure. In configuration, the bigger A^{3+} cation is surrounded by two O (8b) and six O (48f) atoms and the smaller B^{4+} cation is surrounded by six O (48f) atoms in a distorted octahedron. Here, the 48f oxygen atom is coordinated to two A^{3+} and two B^{4+} sites, while the 8b oxygen atom is contained within an A^{3+} cation-formed tetrahedron.

In particular, hardness is one of the most important physical parameters that characterizes the mechanical properties of materials. Vicker's micro-hardness has been shown correlated nicely with the strength and bulk modulus in numerous materials [20,21]. On the basis of chemical bonds and effect of valence d-electrons, the hardness of covalent compounds studied by Guo et al. [22]. Jhi and other workers [23] have developed the correlation between valence electrons concentrations and hardness for semiconducting materials. Recently, Yang et al. [24] have studied the physical parameters of $La_2B_2O_7$ (B =Zr, Sn, Hf, Ge) pyrochlores using First-principles techniques. Feng et al. [25] have reported the electronic structure, mechanical properties and thermal conductivity of $Ln_2Zr_2O_7$ (Ln =La, Pr, Nd, Sm, Eu, Gd) pyrochlores employing the local-density approximation (LDA) of spin polarized scheme +U calculations and next to it verified by experimental results and confirm that studied compounds are promising thermal barrier coating (TBC) materials. However, studies of $Ln_2B_2O_7$ (B = Hf, Ge, Ru, Ir) with pyrochlore structures are still insufficient.

Recently, theoretical studies rely on empirical relationships becomes a crucial component of crystallography study. The empirical relationships have always been evolved as a uncomplicated, ready to use, and to produce improved outcomes for physical parameters. Empirical relationships are most often accepted as the preferred technique for computational solid-state investigations. In earlier researches, author and co-workers have been reported the structural, mechanical and electronic properties of zinc-blende and rock-salt structured binary and ternary tetrahedral chalcopyrite semiconductors using various methods successfully [26-34]. Even though empirical relations frequently don't produce incredibly accurate answers for each unique substance, they can nevertheless be extremely helpful. To the best of my knowledge, mechanical property, particularly Vicker's hardness, has not been studied theoretically using POT of solids in rare earth pyrochlore oxides, till date. Therefore, to bridge this gap, it would be interesting to offer a different rationale for the vicker's hardness of cubic-structured pyrochlore oxides. Herein, a model obtained from POT of solids is being put forward to investigate the mechanical properties of rare earth pyrochlore oxides. It is now widely accepted that a metal's plasmon energy changes [28-35], when it combines chemically to create a compound, conduction electrons in a metal are collectively excited to form plasma of energy $\hbar\omega_p$.This energy depends upon the density of conduction band. Hence the plasmon energy is affected by the density of conduction electrons as well as effective number of valence electrons, both of which change in the formation of compound.

In present work, the relationship between vicker's hardness and plasmon energy for the cubic structured pyrochlore oxides $(A_2^{+3}B_2^{+4}O_7)$ (A = La→Lu, Y & B = Sn, Ti, Zr, Hf, Ge, Ru, Ir) has been discussed employing the plasma oscillation theory (POT) of valence electrons in solids. In investigation of hardness, effect of valence d-electrons of the metal has been taken into account and the obtained values of vicker's hardness is in compliance with available experimental data as compared to previous theoretical investigations on the same. This model divulges vicker's hardness unprecedentedly and accurately for many pyrochlores.

2. THEORETICAL FORMALISM OF HARDNESS

The hardness as a characteristic of pyrochlore crystals has been proved a crucial physical parameter, which determines the bond strengths in these crystals. The term hardness refers to stiffness or temper, resistance to scratching, abrasion, or cutting. The elastic and plastic deformation characteristics of solid materials are usually related to hardness. The metal handbook defines the hardness; the resistance of a material to plastic deformation is measured by its hardness. A true scientific definition of hardness has yet to come. This is due to the fact that hardness is influenced by a variety of factors. As a result, a number of different hardness measurement methods have been evolved. Hardness is a mechanical property that delineates not only the state of material under consideration, but also some deeper basic features of the material, such as the chemical bonding character. Many theoretical approaches to determining the hardness of solids have been presented. Among them Vicker's and Knoop hardness scales are most often used to measure this mechanical parameter. However, it is not remarkable that only the resultant force per unit area could play a key role in determining the hardness of the materials. Since, the hardness of the metal and compound is determined by the energy of the quanta in plasma oscillations of the valence electrons and is given as [35-36],

From the classical consideration, we get the frequency of plasmon oscillations as

$$\omega_p = (4\pi N_e e^2/m)^{0.5}$$

Hence the amount of energy given to plasmon becomes

$$\hbar\omega_p = \hbar\,(4\pi N_e e^2/m)^{0.5} \tag{1}$$

Here $\hbar\omega_p$ is the plasmon energy, N_e-effective no. of free electrons per unit volume participating in plasma oscillations; *e*-electronic charge and *m*-mass of an electron.

For a compound, the plasmon energy in Eq. (1) may also be defined as [36]

$$\hbar\omega_\mathrm{p} = 28.8\ (\mathrm{Z}\sigma/\mathrm{W})^{0.5} \tag{2}$$

Eq. (2) is valid for free electrons and up to first approximation. It can be employed for insulators and semiconductors. During last four decades, Kumar [37] has explored the relationships for electronic properties of chalcopyrite solids in term of plasmon energy. Gupta et al [34] and Verma et al [38] have established a relationships between the mechanical properties and melting point, inter-atomic distance and iconicity of the compounds.

Verma et al. [38] have developed an empirical relation between micro-hardness and bulk modulus for tetragonal structured chalcopyrite solids as follows

$$\mathrm{H} = \mathrm{KB}^{\mathrm{K}+1} \tag{4}$$

where K is crystal structure dependent constant with values of 0.50 and 0.59 for $\mathrm{I-III-VI_2}$ and $\mathrm{II-IV-V_2}$ chalcopyrites, respectively.

Previously, many researchers have studied the static, dynamical, optical, mechanical and electronic properties of binary and ternary chalcopyrites semiconductors, and rare earth chalcogenides using empirical models based on plasmon oscillation theory of solids [28-34]. As per above study, the mechanical properties of pyrochlores have a fundamental relationship between hardness H and plasmon energy $\hbar\omega_p$.

Physical parameters are obviously important for device development, but no one has demonstrated meaningful results on Vicker's hardness using various approaches. As, this modulus is much valance electrons dependent. Hence, we tried a new empirical approach to come across accurate results close to experimental values using plasmon energy of compound.

The experimental vicker's hardness $\mathrm{H_v}$ [GPa] of these pyrochlores shows linearity when plotted a graph with respect to plasmon energy $(\hbar\omega_\mathrm{p})^{3/4}$ and presented in Figure 2.2. It is noteworthy that the method of determining bulk modulus by this mechanism creates a difference from experimental techniques, and this could develop errors.

It is macro and micro changes in the compounds characteristic which leads to mechanical changes; here, it is plasmon energy of valance electrons that defines this macro and micro change in the compound. As a result, a linear regression line is plotted for the vicker's hardness, which results in an expression of vicker's hardness [GPa] as;

$$\mathrm{H_v} = \mathrm{P} + \mathrm{Q} \times \left(\hbar\omega_\mathrm{p}\right)^{3/4} \tag{5}$$

Here constants P and Q, and regression coefficient R are presented in Table 1. In this table probability parameter S shows the significance of regression as null i.e. there is no correlation.

Table 1. Ternary tetrahedral semiconductors data gives the following linear regression result.

Property	P	Q	R	S
Vicker's Hardness	-84.6281±10.4998	9.6743±1.0566	0.9660	<0.0001

A detailed study of elastic properties such as hardness of complex structured pyrochlores, covalent crystals and binary solids has been given elsewhere [34, 35] and will not be discussed here. The properties of $A_2B_2O_7$ pyrochlore compounds have been thoroughly studied and some of these materials have been noticed for practical applications [4-10]. The information about elastic properties of pyrochlores such as hardness is rather incomplete and experimental data found only for few pyrochlores. This study suggests the elastic properties in more accurate manner.

3. RESULT AND DISCUSSION

In the present study, it is shown that empirical relationship exists for pyrochlores and this can be successfully employed to investigate the hardness from their plasmon energy as a key parameter.

The investigated values of hardness of these materials have been given in Table 2 and weighed against the available experimental data and other such theoretical investigations reported so far. Vicker's hardness of these crystals exhibits a linear relationship when plotted against their Plasmon energy $\hbar\omega_\mathrm{p}$ (in eV), which are calculated using the relation (2) and falls on a straight line. From Fig. 2.1, it is obvious that the hardness follows rising trends in these compounds with their increasing plasma energy.

It can be seen that the values of hardness computed from this proposed empirical relation is in better conformity with experimental data in comparison to the values reported by earlier workers. As an illustration the results obtained for $\mathrm{H_v}$ (in GPa) vary from experimental values by the amount as follows: 1.43% for $La_2Sn_2O_7$, 0.20% for $Nd_2Sn_2O_7$, 0.86% for $Sm_2Sn_2O_7$, 1.44% for $Gd_2Sn_2O_7$, 3.61% for $Er_2Sn_2O_7$, 4.50% for $La_2Zr_2O_7$, 1.67% for $Pr_2Zr_2O_7$, 7.33% for $Nd_2Zr_2O_7$, 5.77% for $Sm_2Zr_2O_7$ and 13.67% for $Eu_2Zr_2O_7$. A few higher deviations of hardness values in these compounds are owing to larger bond lengths. With increasing bond length, plasmon energy decreases, which widen the variance of these results. Another reason for greater deviations of hardness values is unit cells mismatch between substrate and deposited films. Explicitly hardness of ternary compounds is more sensitive with plasmon energy as observed in calculated values.

Table 2: Calculated values of vicker's hardness H_v (in GPa) of pyrochlores.

$A_2B_2O_7$	$\hbar\omega_p$ (eV) [Eq. 2]	Vicker's Hardness (Hv) Cal. [Eq. 5]	Vicker's Hardness (Hv) Expt. [4,25]	Vicker's Hardness (Hv) Reported [4, 13, 25]
$La_2Sn_2O_7$	21.051	10.449	10.6±0.2	14, 14.9
$Ce_2Sn_2O_7$	21.091	10.584		
$Pr_2Sn_2O_7$	21.202	10.960		
$Nd_2Sn_2O_7$	21.280	11.223	11.20±0.4	16.00
$Sm_2Sn_2O_7$	21.571	12.205	12.10±0.6	16.60
$Eu_2Sn_2O_7$	21.660	12.504		
$Gd_2Sn_2O_7$	21.682	12.578	12.40±0.2	16.70
$Tb_2Sn_2O_7$	21.771	12.877		
$Dy_2Sn_2O_7$	21.862	13.183		
$Ho_2Sn_2O_7$	21.960	13.511		
$Er_2Sn_2O_7$	22.070	13.880	14.40±0.3	17.90
$Tm_2Sn_2O_7$	22.132	14.087		
$Yb_2Sn_2O_7$	22.240	14.448		
$Lu_2Sn_2O_7$	22.301	14.652		
$Y_2Sn_2O_7$	22.320	14.716		
$La_2Ti_2O_7$	21.980	13.578		
$Sm_2Ti_2O_7$	22.051	13.816		
$Eu_2Ti_2O_7$	22.161	14.184		
$Gd_2Ti_2O_7$	22.180	14.248		
$Tb_2Ti_2O_7$	22.212	14.355		
$Dy_2Ti_2O_7$	22.293	14.625		
$Ho_2Ti_2O_7$	22.346	14.802		
$Er_2Ti_2O_7$	22.556	15.502		
$Tm_2Ti_2O_7$	22.615	15.699		
$Yb_2Ti_2O_7$	22.568	15.542		
$Lu_2Ti_2O_7$	22.683	15.925		
$Y_2Ti_2O_7$	22.791	16.284		
$La_2Zr_2O_7$	20.758	9.454	9.90	8.90, 9.80
$Ce_2Zr_2O_7$	20.964	10.154		
$Pr_2Zr_2O_7$	21.088	10.574	10.40	12.10
$Nd_2Zr_2O_7$	21.135	10.733	10.00	11.70
$Sm_2Zr_2O_7$	21.402	11.635	11.00	10.70
$Eu_2Zr_2O_7$	21.491	11.935	10.50	9.60
$Gd_2Zr_2O_7$	21.583	12.245	10.00	12.30
$Tb_2Zr_2O_7$	21.743	12.783		
$Dy_2Zr_2O_7$	21.825	13.059		
$Ho_2Zr_2O_7$	21.922	13.384		
$Er_2Zr_2O_7$	21.998	13.639		
$Tm_2Zr_2O_7$	22.084	13.927		
$Yb_2Zr_2O_7$	22.187	14.271		
$Y_2Zr_2O_7$	21.792	12.948		
$La_2Hf_2O_7$	20.848	9.760		8.90
$Ce_2Hf_2O_7$	21.210	10.987		
$Pr_2Hf_2O_7$	21.246	11.108		
$Nd_2Hf_2O_7$	21.267	11.179		
$Sm_2Hf_2O_7$	21.469	11.861		
$Eu_2Hf_2O_7$	22.110	14.014		
$Gd_2Hf_2O_7$	21.610	12.336		
$Tb_2Hf_2O_7$	21.765	12.857		
$Dy_2Hf_2O_7$	21.891	13.280		
$Ho_2Hf_2O_7$	21.998	13.639		
$Er_2Hf_2O_7$	22.094	13.960		
$Tm_2Hf_2O_7$	22.183	14.258		
$Yb_2Hf_2O_7$	22.254	14.495		
$Lu_2Hf_2O_7$	22.345	14.799		
$Y_2Hf_2O_7$	22.319	14.712		
$Pr_2Ru_2O_7$	22.055	12.44		
$Nd_2Ru_2O_7$	22.616	12.75		
$Sm_2Ru_2O_7$	22.391	13.09		
$Eu_2Ru_2O_7$	22.460	13.22		
$Gd_2Ru_2O_7$	22.539	13.38		
$Tb_2Ru_2O_7$	22.612	13.52		
$Dy_2Ru_2O_7$	22.759	13.82		
$Ho_2Ru_2O_7$	22.793	1389		
$Er_2Ru_2O_7$	22.908	14.12		
$Tm_2Ru_2O_7$	22.976	14.26		
$Yb_2Ru_2O_7$	23.055	14.43		
$Lu_2Ru_2O_7$	23.041	14.40		
$Pr_2Ir_2O_7$	21.963	12.27		
$Nd_2Ir_2O_7$	22.023	12.38		
$Sm_2Ir_2O_7$	22.284	12.88		
$Eu_2Ir_2O_7$	22.297	12.90		
$Gd_2Ir_2O_7$	22.414	13.13		
$Tb_2Ir_2O_7$	22.559	13.42		
$Dy_2Ir_2O_7$	22.612	13.52		
$Ho_2Ir_2O_7$	22.689	13.68		
$Er_2Ir_2O_7$	22.772	13.85		
$Tm_2Ir_2O_7$	22.847	14.00		
$Yb_2Ir_2O_7$	22.918	14.15		
$Lu_2Ir_2O_7$	22.987	14.29		
$La_2Ge_2O_7$	22.667	13.64		18.3
$Bi_2Pt_2O_7$	22.105	12.54		
$Bi_2Rh_2O_7$	22.644	13.59		
$Bi_2Os_2O_7$	22.173	12.67		
$Bi_2Ru_2O_7$	22.560	13.42		
$Bi_2Ir_2O_7$	22.465	13.23		
$Bi_2Ti_2O_7$	22.121	12.57		

Hence, it is clear from these results that the proposed empirical model is quite reasonable and can give us full insight for investigation and predicting the elastic properties of these materials.

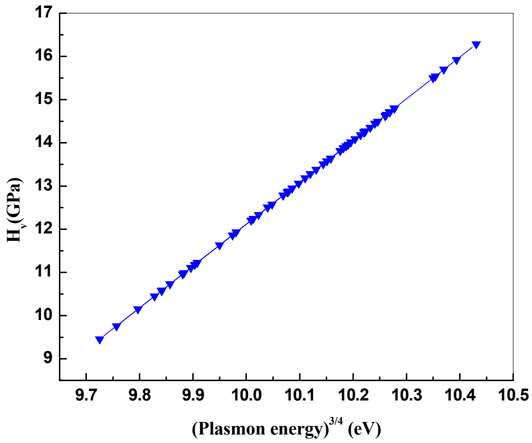

Figure 2.1. Calculated H_V [GPa] versus Plasmon energy for pyrochlore compounds. Vicker's hardness of pyrochlores lies on a striaght line and shows increasing trend.

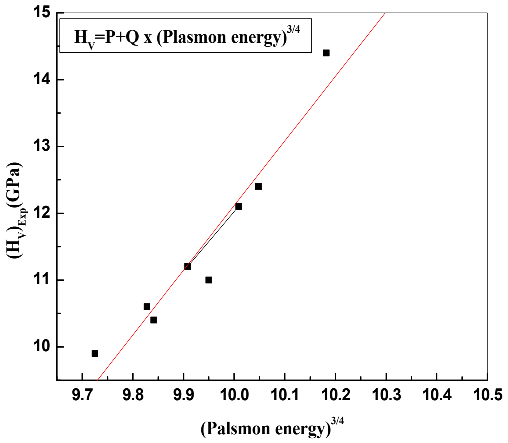

Figure 2.2. Experimental H_V [GPa] versus Plasmon energy for pyrochlore compounds. This straight line exhibits a linear relationship obtained by regression analysis of data. Experimental data are taken from [4, 25].

4. CONCLUSION

According to above results and discussions attained by employing the extended empirical relation, plasma energy of the valence electrons is key parameter for investigating the mechanical/elastic properties of pyrochlore structured solids. In the current investigation, estimates varied somewhat from experimental data by 0.20% to 13.67%. The obtained results express a continuous tendency and are commensurate with the already revealed results reported so far, this confirms the viability of the suggested method. The predicted values of studied compounds are cited in the Table 2. Hence it is clear that such theory can be easily extended to pyrochlore crystals and excellent agreement was found between estimated and the experimental data as compared to other such reported theoretical investigations, previously. In this manner, this model is pioneer in determining the hardness of most of the compounds with the plasmon energy, which assists to determine other crucial properties for technological applications. Furthermore, it is found that in these crystals (investigated), hardness of $A_2B_2O_7$ crystals shows a linear relationship, when plotted against plasma energy of their valance electrons. Hence, it makes sense to state that such empirical model can be easily unfolded to perovskite structured solids to determine their elastic properties; the work on the project is ongoing, and it will be reported in upcoming articles.

CRediT authorship contribution statement:
Rekha Bhati: Investigation, Methodology, Writing- original draft. **Dheerandra Singh Yadav:** Data curation, **Preeti Varshney:** Conceptualization, **Rajesh Chandra Gupta:** Visualization, **Ajay Singh Verma:** Supervision, Writing-review & editing.

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НАПІВЕМПІРИЧНІ ПЕРЕДБАЧЕННЯ ТВЕРДОСТІ РІДКІСНОЗЕМЕЛЬНИХ ПІРОХЛОРІВ; ДІЕЛЕКТРИКИ З ВИСОКОЮ ПРОНИКНІСТЮ ТА МАТЕРІАЛИ ДЛЯ ТЕРМОЗАХИСНИХ ПОКРИТТІВ

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В роботі сформульована спрощена напівемпірична модель твердості за Віккером рідкоземельних пірохлорних сполук. Ми розглянули $A_2^{+3}B_2^{+4}O_7$ структурованих 97 пірохлорних сполук для розрахунків твердості за Віккером. Енергія плазмону ($\hbar\omega_p$) залежить від основних параметрів матеріалу, таких як N_e-ефективне число вільних електронів на одиницю об'єму, які беруть участь у коливаннях плазми, e-електронний заряд і m-маса електрона. Запропонована модель передбачає, що експериментальні та теоретичні значення твердості за Віккером зростають із збільшенням плазмонної енергії пірохлору. Ми виявили, що розраховані значення краще узгоджуються з наявними експериментальними та теоретичними даними, що підтверджує достовірність моделі. Ця модель підтримує моделювання нових функціональних пірохлорних сполук і допомагає зрозуміти їхні механічні властивості: відмінна термічна стабільність, надпровідність, батареї, сегнетоелектрика, розкидання води, висока іонна провідність, хороша фотолюмінесценція, властиві кисневі вакансії, екзотичний магнетизм і важлива для сьогодення для інкапсуляції ядерних відходів та аерокосмічної промисловості.

Ключові слова: *пірохлори; плазмонна енергія; твердість за Віккером*