

SUPPLEMENTARY INFORMATION for

Electronic, optical and thermoelectric properties of PrMO₃ (M = Al, Ga, In) from first-principles calculations

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ESI 1. COMPUTATIONAL DETAILS

The exchange-correlation potential was treated by the generalized gradient approximation (GGA) as proposed by Perdew-Burke-Ernzerhof [1-2] in both the computational methods. We used the simplified, rotationally invariant approach introduced by Dudarev *et al* [3] to take into account the strong on-site Coulomb repulsion amongst the localized Pr 4f electrons. The effective Coulomb potential ($U_{\text{eff}} = U - J = 5.5$ eV, where $U = 6.5$ eV and $J = 1$ eV) [4] was applied for the f-state of Pr in both VASP [5] as well as Wien 2k [6] calculations. The structural optimization was performed using the conjugate gradient algorithm [7]. In order to obtain the ground state structure, the lattice parameters, ionic positions and the shape of the unit-cell were relaxed until the pressure on the optimized structure was almost zero and the Hellmann-Feynman forces were less than 0.01 eV/Å using the projector augmented wave (PAW) [8-9] formalism as implemented in VASP [5]. All the calculations were then performed with this relaxed structure. The plane wave cut-off energy of 500 eV and $6 \times 6 \times 4$ k mesh were used to achieve reasonable convergence. The sampling integration over the Brillouin zone was employed using the Monkhorst-Pack method [10]. The Fermi surface was treated by the Methfessel-Paxton [11] method with a smearing of 0.5 eV. For WIEN 2k calculations the multi-pole expansion of the crystal potential and the electron density within the muffin tin (MT) spheres were cut at $l = 10$. The R_{MT} (muffin-tin radius) was selected to be 2.13, 1.80, and 1.54 au for Pr, Al, and O elements respectively in the case of PAO compound. For PGO the R_{MT} was 2.12, 1.87, and 1.47 au for Pr, Ga, and O respectively and 2.33, 2.09, 1.79 au for Pr, In, and O respectively, for the compound PIO. Non-spherical contributions to the charge density and potential within the MT spheres were considered up to $l_{\text{max}} = 6$. The cut-off parameter $R_{\text{MT}} \times K_{\text{max}} = 7$ was chosen, which controls the convergence of the basis set (K_{max} is the plane-wave cut off). The convergence criterion was set to be 10^{-4} Ry. The core states were treated relativistically, the semi-core states were treated semi-relativistically, i.e., ignoring the spin-orbit (SO) coupling. The energy cut-off between the core and the valence states was set at -8.0 Ry.

ESI 2. OPTICAL PROPERTIES

The linear response of a material to an external electromagnetic field with a small wave vector is measured through the complex dielectric function $\epsilon(\omega)$. Since we are keen on understanding the optical response of the material, the frequencies of our interests lie in the optical frequency range, viz., 10^{13} - 10^{16} Hz. Time-dependent perturbations of the ground electronic states can be used to depict the interaction of photon (which is associated with the electromagnetic field) and the electrons of the material. The subsequent optical transitions between the occupied and the unoccupied electronic states that occur because of the electric field of the photon give rise to the observed optical spectra. Optical spectra can in this manner be expressed in terms of the joint density of states between the valence band (VB) and the conduction band (CB). Eigen vectors obtained from the solution of the Schrodinger equation can give the VB and CB, which are then used to obtain the momentum matrix elements and finally the complex dielectric function [12]. The imaginary part of the complex dielectric function can thus be written as [13]

$$\epsilon_2^{ij} = \frac{4\pi^2 e^2}{Vm^2 \omega^2} \times \sum_{nn'\sigma} \langle kn\sigma | p_i | kn'\sigma \rangle \langle kn'\sigma | p_j | kn\sigma \rangle \\ \times f_{kn} (1 - f_{kn'}) \delta(E_{kn'} - E_{kn} - \hbar\omega)$$

where e is the charge and m is the mass of the electron, the symbols ω and V represent the angular frequency of electromagnetic radiation striking the crystal, and unit cell volume respectively. $|kn\sigma\rangle$ represents the crystal wave function with crystal momentum k , and σ spin stands for the eigen value E_{kn} that corresponds to the momentum operator p_j . The Fermi distribution function (f_{kn}) identifies the transition from the occupied to the unoccupied state and $\delta(E_{kn'} - E_{kn} - \hbar\omega)$ shows the total energy conservation.

In order to compute the optical properties the Brillouin zone integration was performed with a dense mesh of uniformly distributed $24 \times 17 \times 24$ k -mesh in the Brillouin zone, which corresponds to 1296 k points in the irreducible Brillouin zone. The symmetry group of the studied compounds has two dominant components of the dielectric tensor, corresponding to the electric field perpendicular and parallel to the optical c -axis, which completely characterizes the linear optical properties. These are $\epsilon_2^{xx}(\omega)$ and $\epsilon_2^{zz}(\omega)$, i.e., the

imaginary parts of the frequency dependent dielectric function. The real part of the dielectric function $\varepsilon_1(\omega)$ can then be derived from the imaginary part using the Kramers-Kronig relation,

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'$$

where P implies the principal value of the integral. The knowledge of both the $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ can be used to calculate some important optical functions such as refractive index, reflectivity, and absorption coefficients.

REFERENCES

- 1 J.P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77** 3865-3868.
- 2 J.P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 1997, **78** 1396 Erratum.
- 3 S.L. Dudarev, G.A. Botton, Y.Y. Savrasov, C.J. Humphreys and A.P. Sutton, *Phys Rev. B* 1998, 57 1505.
- 4 W. Setyawan and S. Curtarolo, *Comp. Mater. Sci.* 2010, **49** 299-312.
- 5 G. Kresse and J. Furthmuller, *Phys. Rev. B* 1996, **54** 11169- 11186.
- 6 P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, J. Luitz and K. Schwarz, *An Augmented Plane Wave plus Local Orbitals Program for Calculating Crystal Properties. Wien2K Users Guide*, Wien Techn. Universitat Austria (2008).
- 7 W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vetterling, *Numerical recipes: The Art of Scientific Computing*, Cambridge University Press, New York, 1986.
- 8 P.E. Blöchl, *Phys. Rev. B.* 1994, **50** 17953–17979.
- 9 G. Kresse and D. Joubert, *Phys. Rev. B* 1999, **59** 1758–1775.
- 10 H.J. Monkhorst and J.D. Pack, *Phys. Rev. B* 1976, **13** 5188- 5192.
- 11 M. Methfessel and A.T. Paxton, *Phys. Rev. B* 1989, **40** 3616.
- 12 A. Roy, R. Prasad, S. Auluck and A. Garg, *Journal of Applied Physics* 2014, **115** 133509.
- 13 F. Bassani and G.P. Parravicini, *Electronic states and optical transitions in solids*. Pergamon Press Ltd., Oxford, 1975 p 149.