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The Electronic Band Structure and Linear Optical Properties of Bilayer MoS_2 and $MoSe_2$

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Abstract

We have performed first principle pseudopotential calculations of the electronic band structure and linear optical properties of bilayer MoS_2 and $MoSe_2$ using density functional-Hartree-Fock theory. Our results reveal that both bilayer MoS_2 and $MoSe_2$ are semiconductors with direct band gap. The optical spectra for both materials are similar and they show the two major excitonic transition which is a feature of M-CH_2.

1.0 Introduction

The disulphidies and diselenides of Molybdenum form a class of semiconducting layered transition-metal dichalcogenides (M-CH_2) compounds with a trigonal prismatic coordination of the metal atoms. They exist in two crystalline forms, hexagonal and rhombohedral. Molybdenum disulfide (MoS_2) and Molybdenum diselenides ($MoSe_2$) is one of the best known solid lubricants, and although it originally gained popularity in aerospace and military applications, it is now commonly found in a variety of lubrication applications. It is widely used in greases and specialized grease-like products known as pastes, in fluid lubricants such as automotive and industrial gear oils, in solid film lubricants including but not limited to burnished (rubbed-on) films, sputtered coatings, resin bonded and impingement coatings and solar cells (Jäger-Waldau et al, 1991; Epshteyn and Risdon**,** 2010).

The bulk band structure and optical properties of these materials has been well studied both experimentally and theoretically (Wilson and Yoffe ,1969; McMenamin and Spicer, 1972; Kam and Parkinson, 1982; Kam et al, 1984; Kasowski, 1973; Bullett, 1978; Coehoorn et al, 1987a ; Coehoorn et al, 1987b ; Matheiss, 1973; Wood and pendry, 1973). The nanostructured form of the layered compound $MoSe_2$ and MoS_2 have received much attention due to their potential as catalysts for desulferization of crude oil and photo-electrochemical hydrogen evolution (Olsen et al, 2011).

The band structure and absorption spectrum of monolayer MoS_2 have also been studied theoretically and experimentally (Olsen et al, 2011; Mak et al, 2010; Kobayashi and Yamauchi, 1995; Frey et al, 1998 and Lebègue and Erikssen, 2009). Optical measurement of $MoSe_2$ monolayer have also been studied (Jäger-Waldau et al, 1991; Mallouky and Bernarede, 1988 and Bichsel and Lévy, 1984). The bilayers of the materials under investigation have not received much attention. Olsen et al (2011) in their bilayer calculation using GW approximation obtained an indirect band gap of 1.2 eV. Mak et al, 2010 in their experimental setup obtained a band gap value of 1.6 eV.

In this paper we present the electronic band structure and linear optical response of bilayer MoS_2 and $MoSe_2$.

2.0 Method

We have investigated the electronic band structure of multilayer $MoSe_2$ and MoS_2 utilizing Hartree-Fock-DFT scheme in Abinit packages (Gonze et al, 2002; Gonze et al, 2005). For exchange and correlation, the generalized gradient approximation (GGA) as parametrized by Perdew-Burke-Ernzerhof (1996) was used in the calculation. A kinetic energy cut-off of 10 Hartree was used for the plane wave expansion. In the self-consistency calculation for the bilayer material a k-point grid of 10x10 was used for the IBZ integration while for the bulk a k point mesh of 64 was used. The self-

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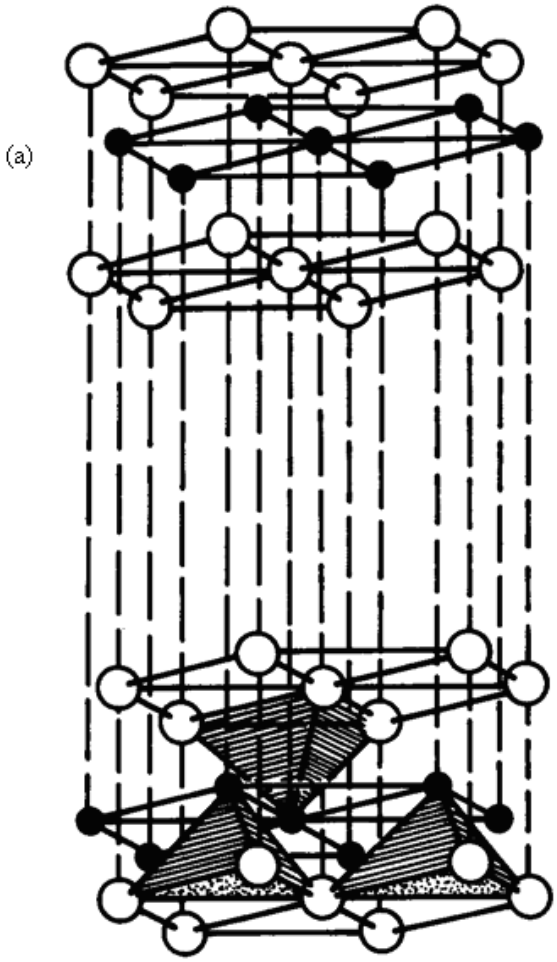
consistency criterion on the energy was $1.0x10^{-6}$. A separation of 29.3 Å was used for the bilayer calculation.

We have also performed linear optical response (Sharma and Ambrosch-Draxl, 2004) calculations for the materials under investigation. The linear properties were calculated on a k-point mesh of 1600 in the IBZ. The calculation was scissors (the difference in energy between the LDA and HF was added to the calculation to induce a shift of the conduction band) corrected.

$MoSe_2$ and MoS_2 crystallize in the hexagonal 2H-MoS_2 structure with space group $P6_3/mmc$ which corresponds to number 194 in the international tables of Crystallography. The 2H-MoS_2 (2H-$MoSe_2$) structure is shown in Figure 1. Detail of the lattice parameters are given in table 1.

Table 1: Input parameters taken from (Coehoorn et al, 1987)

Lattice constant (Å)	MoS_2	$MoSe_2$
a	3.1604	3.288
c	12.295	12.900



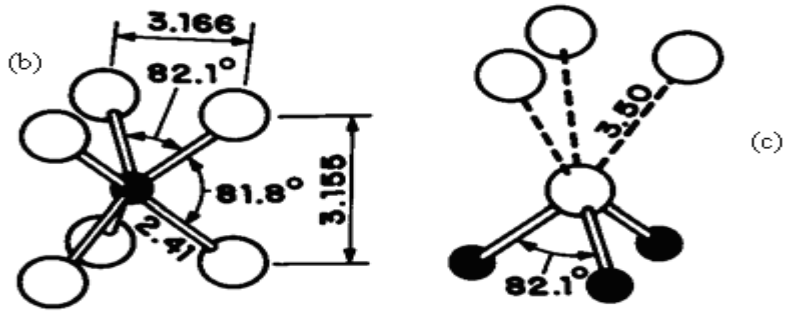


Figure 1. The crystal structure of MoS_2. and $MoSe_2$ Molybdenum atoms are small filled circles; sulfur or Se atoms are large open circles (b) Configuration of MoS2 trigonal prism (c) surroundings of sulfur atom. Mo and S or Se are shown by solid and open circles respectively.

3.0 Results And Discussion

The result of the bulk calculation of the electronic band structure of $MoSe_2$ is shown in Figure 2. The band structure of bulk MoS_2 is not shown since it is similar to that of $MoSe_2$ and because we only included it for the purpose of comparison. The plot is along lines of high symmetry of the first irreducible brilluioun zone (BZ). The valence band minimum (VMB) is at the K point of high symmetry while the conduction band minimum (CBM) is at the M point. The fundamental band gaps are indirect which agrees with the results of (Olsen et al, 2011; Coehoorn *et al*, 1987a; Kobayashi and Yamauchi, 1995; Frey et al, 1998; Huisman et al, 1971; McMenamin and Spicer, 1972), but shows disagreement as regard the VBM. Our VBM show agreement with the results of Matheiss (1973) and Wood and pendry (1973). The value of the indirect band gap for bulk MoS_2 from our calculation is 0.81 eV. The experimental indirect band gap value for $MoSe_2$ ranges from 1.19-1.45 eV (Jäger-Waldau et al, 1991).

The electronic band structure of bilayer (two slab) MoS_2 and $MoSe_2$ are presented in Figures 3 and 4 respectively. The plot is along lines of high symmetry in the first Brillouin zone of the hexagonal close pack (HCP). Like in the bulk calculations, the VBM is at the K point for both materials while the bottom of the CBM is at the M point. The energy band gap is direct with a value of 1.42 eV for both materials. This is in agreement with the experimental results of Mak et al (2010) who observed a transition from an indirect to direct band gap when going from a few layers to mono-layer. But in this work, a direct band gap have been observed. Kobayashi and Yamauchi (1995) in their surface calculation of molybdenum dichalcogenide used three and four monolayers in the calculations and observed indirect band gap. The 4d orbital of the Mo atom is made up of five shells which are grouped into the e_g and the t_{2g} character which corresponds to the occupied and unoccupied shells of the 4d orbital. This implies that the top of the valence band is made up of Mo 4d state while the bottom of the conduction band is dominated by Mo 4d band. The band structures for both materials are similar.

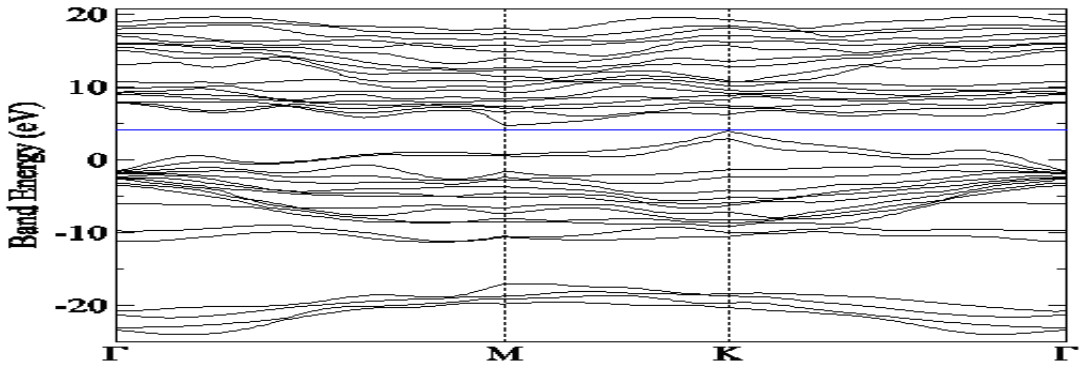


Figure 2: The electronic band structure of bulk $MoSe_2$ (LDA). The Fermi energy is indicates by the thick horizontal line. A band gap of 0.81 eV was obtained.

The calculated imaginary parts of the dielectric functions for bilayer $MoSe_2$ up to photon energy of 15 eV are shown in Figures 5 and 6. In order to study the optical anisotropy in the bilayer $MoSe_2$, the calculated imaginary part of the dielectric functions is resolved into two components $\varepsilon_i^{xy}(\omega)$ and $\varepsilon_i^{zz}(\omega)$ which corresponds to the perpendicular and parallel polarizations respectively. Figures 5 and 6 show $\varepsilon_i^{xy}(\omega)$ and $\varepsilon_i^{zz}(\omega)$ respectively. Our calculations show two major peaks which are common feature of all layered transition-metal dichalcogenide (MCH_2). Figures 5 and 6 reveals the anisotropy of the material. The first peak at 1.42 eV indicates the onset of band edge absorption which is a measure of the optical band gap. The height of the first peak of $\varepsilon_i^{zz}(\omega)$ in Figure 5 can reach a value of about 18 which is higher than the height of the first peak of Figure 6 by about 5. This shows good agreement with the results of Mak et al (2010). Beyond the gap, $\varepsilon_i^{zz}(\omega)$ show five peaks which are related to critical points of the band structure (CPBSs), $\varepsilon_i^{xy}(\omega)$ show two CPBSs. The peaks of $\varepsilon_i^{zz}(\omega)$ occur at 5.2 eV, 7.1 eV, 7.8 eV and 9.7 eV, while $\varepsilon_i^{xy}(\omega)$ occur at 1.42 ev and 3.4 eV. The difference in the number of peaks also shows the anisotropy of the material. The strong first peak in the imaginary part of the dielectric functions show that the bilayer of $MoSe_2$ can be used in photonic sensors. And it it associated with the van Hove singularities that are located just above and below the Fermi enrgy.

The real part of the dielectric function $\varepsilon_r(\omega)$ is obtained from the imaginary part using the Kramers-Kronig relation. Figures 7 and 8 shows the components of $\varepsilon_r(\omega)$ in the direction perpendicular and parallel to the c axis respectively. The anisotropy discussed for the imaginary part naturally carries over to the real part.

The calculated real and imaginary part of the dielectric functions for bilayer MoS_2 up to photon energy of 15 eV is presented in Figures 9 to 12. The calculated imaginary part of the dielectric function for the bilayer MoS_2 is resolved into two components $\varepsilon_i^{xy}(\omega)$ and $\varepsilon_i^{xx}(\omega)$ which corresponds to the perpendicular and parallel polarizations respectively. As with $MoSe_2$, to show the anisotropy, we look at the height and numbers of peak in both polarizations. For $\varepsilon_i^{xy}(\omega)$, the height of the first peak is about 9 while the height of $\varepsilon_i^{xx}(\omega)$ is about 13. Again, $\varepsilon_i^{xx}(\omega)$ displayed 5 CPBS while $\varepsilon_i^{xy}(\omega)$ show 2 CPBS. The onset of absorption features is at 1.42 eV. The shape and position of this first peak agrees with the result of Mak et al (2010). The two peaks of $\varepsilon_i^{xy}(\omega)$ are at 1.42 eV and 3.8 eV. $\varepsilon_i^{xx}(\omega)$ shows absorption feature at 1.42 eV and has two major peaks which are the excitonic transitions. The 5 CPBSs are at 1.42 eV, 3.4 eV, 6.0 eV, 6.9 eV and 11.1 eV. The real part of $\varepsilon_r^{xy}(\omega)$ and $\varepsilon_r^{xx}(\omega)$ are shown in Figures 11 and 12, and it also shows the anisotropy of the material.

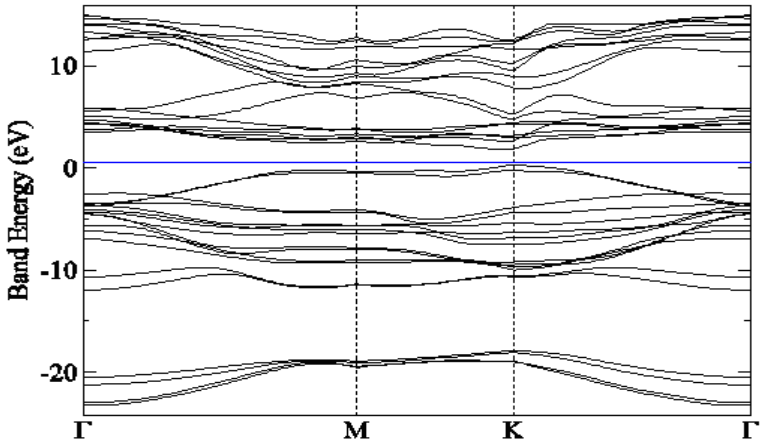


Figure 3: The band structure of bilayer MoS_2. The Fermi energy is indicated by the thick horizontal line is 1.4 eV.

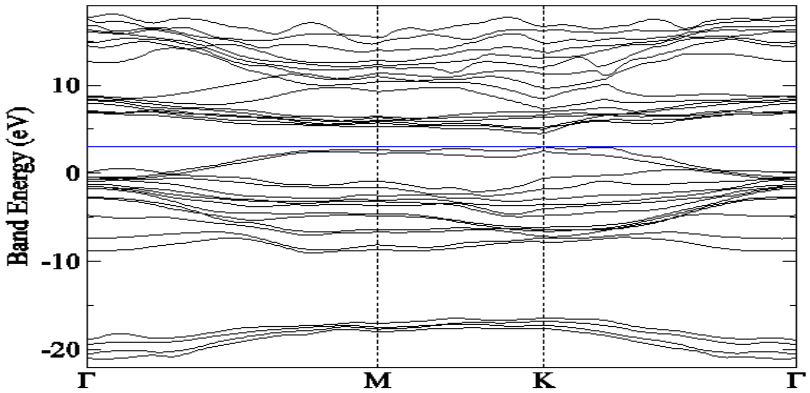


Figure 4: The band structure of bilayer $MoSe_2$. The Fermi energy is indicated by the thick horizontal line. The band gap is 1.4 eV.

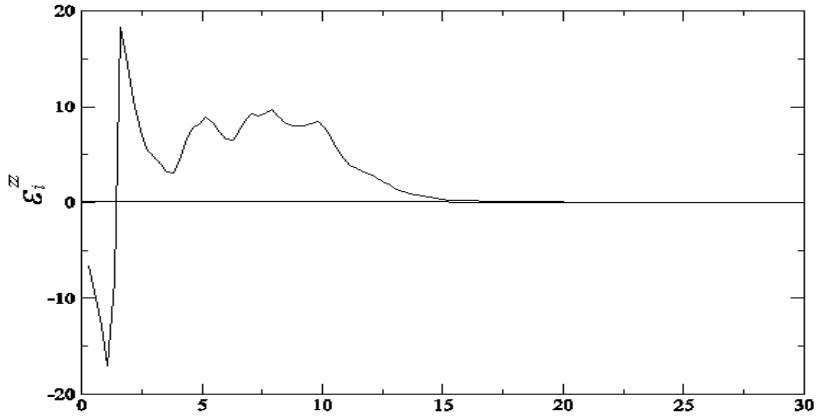


Figure 5: The imaginary part of the dielectric function $\varepsilon_i^{zz}(\omega)$ of bilayer $MoSe_2$ for the parallel polarization.

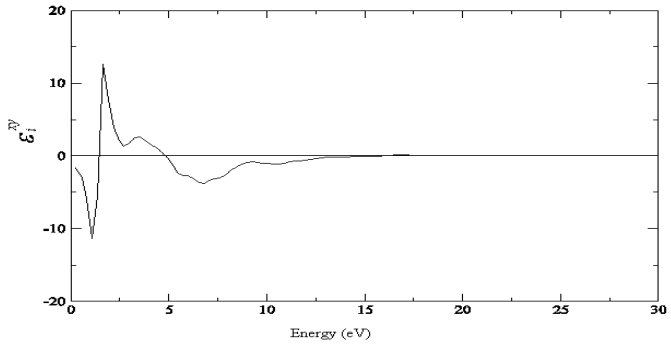


Figure 6: The imaginary part of the dielectric function ε_i^{xy} of bilayer $MoSe_2$ for the perpendicular polarization.

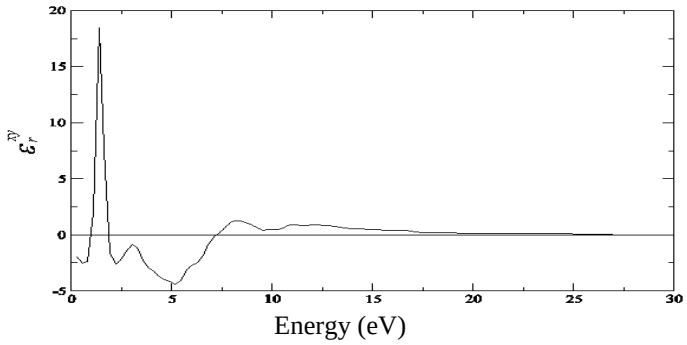


Figure 7: The real part of the dielectric function ε_r^{xy} of bilayer $MoSe_2$ for the perpendicular polarization.

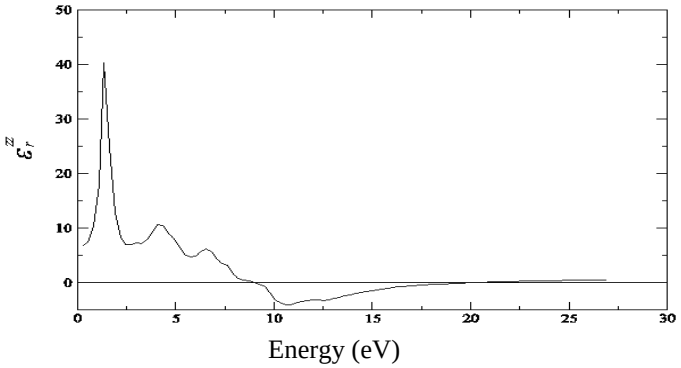


Figure 8: The real part of the dielectric function ε_r^{zz} of bilayer $MoSe_2$ for the parallel polarization.

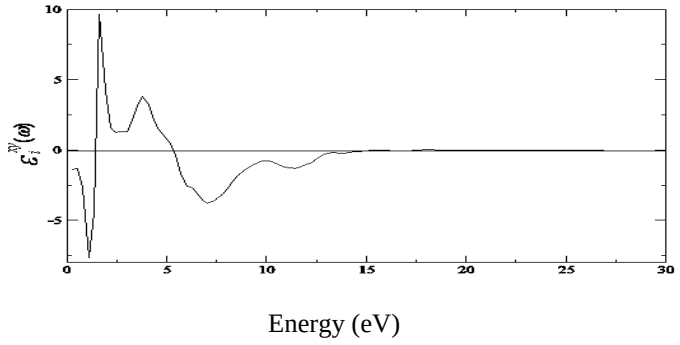


Figure 9: The imaginary part of the dielectric function ε_i^{xy} of bilayer MoS_2 for the perpendicular polarization.

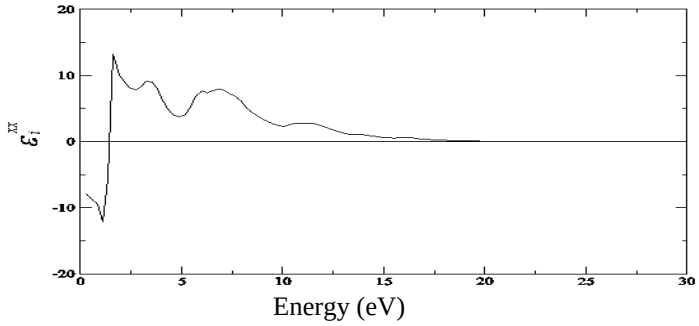


Figure 10: The imaginary part of the dielectric function ε_i^{xx} of bilayer MoS_2 for the perpendicular polarization.

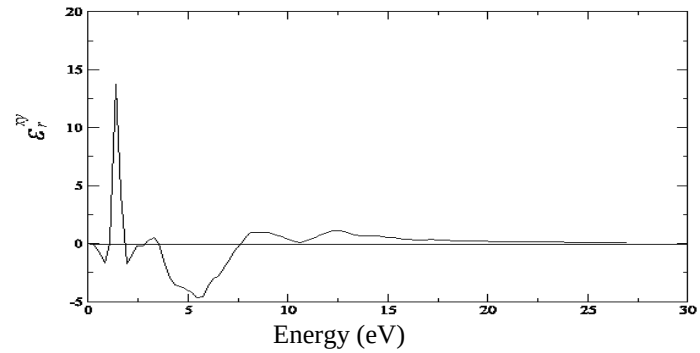


Figure 11: The real part of the dielectric function ε_r^{xy} of bilayer MoS_2 for the perpendicular polarization.

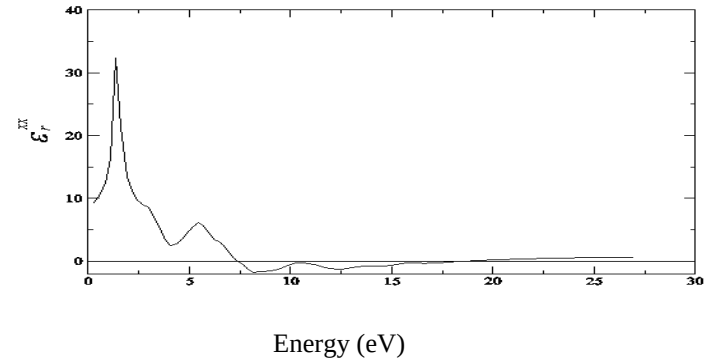


Figure 12: The real part of the dielectric function ε_r^{xx} of bilayer MoS_2 for the perpendicular polarization.

Conclusion

We have performed first principle pseudopotential calculations of the electronic band structure and linear optical properties of bilayer MoS_2 and $MoSe_2$ using DFT-HF method. Our calculations reveal direct band gap for the bilayer MoS_2 and $MoSe_2$ materials with the valence band maximum (VBM) located at the special K point of the Brillouin zone. The optical calculations show two major peaks which are the excitonic transitions. The calculation also reveals the anisotropy of the material along the parallel and perpendicular polarizations. The first strong peak in the imaginary part of the dielectric functions show that the both bilayer material can be use in electro-optical devices.

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