Theoretical and Experimental Study of the Crystal Structures, Lattice Vibrations, and Band Structures of Monazite-Type PbCrO₄, PbSeO₄, SrCrO₄, and SrSeO₄

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ABSTRACT: The crystal structures, lattice vibrations, and electronic band structures of PbCrO₄, PbSeO₄, SrCrO₄, and SrSeO₄ were studied by ab initio calculations, Raman spectroscopy, X-ray diffraction, and optical-absorption measurements. Calculations properly describe the crystal structures of the four compounds, which are isomorphic to the monazite structure and were confirmed by X-ray diffraction. Information is also obtained on the Raman- and IR-active phonons, with all of the vibrational modes assigned. In addition, the band structures and electronic densities of states of the four compounds were determined. All are indirect-gap semiconductors. In particular, chromates are found to have band



gaps smaller than 2.5 eV and selenates higher than 4.3 eV. In the chromates (selenates), the upper part of the valence band is dominated by O 2p states and the lower part of the conduction band is composed primarily of electronic states associated with the Cr 3d and O 2p (Se 4s and O 2p) states. Calculations also show that the band gap of $PbCrO_4$ ($PbSeO_4$) is smaller than the band gap of $SrCrO_4$ ($SrSeO_4$). This phenomenon is caused by Pb states, which, to some extent, also contribute to the top of the valence band and the bottom of the conduction band. The agreement between experiments and calculations is quite good; however, the band gaps are underestimated by calculations, with the exception of the bang gap of $SrCrO_4$, for which theory and calculations agree. Calculations also provide predictions of the bulk modulus of the studied compounds.

1. INTRODUCTION

Recently, there has been a large amount of interest in the study of monazite-type structured oxides. These compounds have importance in areas such as earth, planetary, and materials sciences.^{1–12} Because of their relevance, most of the studies have been focused on monazite-type structured phosphates. Among other oxides, only LaVO₄, PbCrO₄, and CaSeO₄ have been thoroughly studied.^{1,2,6,7,12} For other compounds, like SrCrO₄, PbSeO₄, and SrSeO₄, their crystal structures have been experimentally determined, but few of their Raman-active modes have been measured. In the case of SrCrO₄, attempts have been made to determine the electronic band gap, but values ranging from 2.4 to 2.9 eV can be found in the literature.^{13–15}

Ab initio calculation has shown to be an accurate method to study the physical and chemical properties of $CaSeO_4$ and compounds related to the monazites.¹ Usually, these quantum-mechanical calculations provide an accurate description of these

kinds of oxides, allowing both a better understanding of the experimental results and making accurate predictions. On the basis of this and the facts described above, we consider it timely to perform a theoretical study of PbCrO₄, PbSeO₄, SrCrO₄, and SrSeO₄. X-ray diffraction (XRD), Raman spectroscopy, and optical-absorption experiments were also carried out. The combinations of calculations and experiments have allowed us to systematically study the structural, lattice-dynamics, and electronics properties of the four above-mentioned compounds, making considerable progress in their understanding. The knowledge of the studied properties for the chromates is important for their technological applications.^{16–18} The inclusion of selenates in the study was done with the aim of better understanding the physical properties of the whole family

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of monazite-type oxides. The reported results will be compared with the literature.

The paper is organized as follows: In the next section, we give a detailed description of the experimental techniques. The computational details are presented in section 3. The crystal structures of the four compounds are described together with the vibrational and electronic properties in section 4. Finally, we summarize the results of this work in section 5.

2. EXPERIMENTAL METHODS

SrCrO₄ in powder form was prepared by precipitation by adding 50 mL of a 1 M Sr(NO₃)₂ solution to 50 mL of a 1 M K₂CrO₄ solution. Single crystals were grown using a ternary flux system composed of NaCl, KCl, and CsCl, as described by Schenker et al.¹⁹ The weight composition of the mixture was NaCl (24.8%), KCl (26.4%), CsCl (41.3%), and SrCrO₄ (7.5%). The starting reagents were mixed, placed in a platinum crucible with a tight-fitting lid, and kept for 12 h at 620 °C in a horizontal furnace under an air atmosphere. The melt was slowly cooled first to 530 °C with a temperature gradient of -1.5 °C/h, then to 450 °C at -2 °C/h, and finally to room temperature at -50 °C/h. The crystals were separated by careful dissolution of the flux in deionized water. Yellow single crystals of about 1 \times 1 \times 1 mm³ were obtained.

The PbCrO₄ crystals used for the experiments reported here were obtained from natural crocoite minerals provided by Excalibur Mineral Company. Electron microprobe analysis found that the only impurity present at a detectable level was iron (0.06%). Crystals were translucent with a red-orange color, and their dimensions were about $10 \times 1 \times 1 \text{ mm}^3$.

Powder SrSeO₄ and PbSeO₄ were prepared by precipitation from aqueous solutions of strontium chloride and sodium selenate, and lead acetate and sodium selenate, adapting the synthesis described by Pistorius and Pistorius.²⁰ The strontium chloride solution was prepared by the addition of a 2 M HCl solution (13.6 mL) to a strontium carbonate suspension in water (2.00 g of SrCO₃ in 11.4 mL of H₂O). The lead acetate solution was prepared by dissolving the reagent in water (5.14 g of in 25 mL of H₂O). The sodium selenate solutions were prepared by the addition of water (7.9 mL) and a 2 M sodium hydroxide solution (13.6 mL) to a commercial 40 wt % solution of selenic acid (4.91 g). The selenate solutions was then added dropwise to the strontium and lead solutions, and precipitation occurs. In both cases, the pH of the resulting suspensions was adjusted to be 7–8. The suspensions were then heated at 80 °C for 2 h. The solids were separated by filtration, washed with cold water, and dried in air.

It was confirmed by powder XRD using Cu K α radiation that the PbCrO₄, SrCrO₄, and SrSeO₄ samples are single-phased and present the monazite-type structure (space group $P2_1/n$). Their unit-cell parameters are in very good accordance with those determined by Effenberg and Pertlik from single-crystal XRD experiments.²¹ On the other hand, the XRD pattern of PbSeO₄ corresponds to a mixture of a majority phase, which can be assigned to the monazite-type structure,²¹ and a minority phase, which can be assigned to the and a minority phase, which can be assigned to the β -PbSeO₄ orthorhombic barite-type structure (space group *Pnma*).²² The description of the orthorhombic structure and its relationship with the monazite structure have been described in the literature.² There is a group-subgroup relationship between barite and monazite, and the main difference between them is given by the orientation of the CrO_4 tetrahedra.²³ A more detailed description of the barite-type phases of PbSeO₄ and PbCrO₄ is beyond the scope of this work and can be found in the work by Knight.²³ In spite of the phase coexistence of the synthesized PbSeO₄ powder, after dividing it into small fractions, we have been able to find portions of it in which XRD only detected the monazite-type phase. These samples were used for the experiments described here.

Raman experiments were performed for $SrCrO_4$, $PbSeO_4$, and $SrSeO_4$ in the backscattering geometry using a 532 nm laser with a power of less than 20 mW to avoid sample heating. Laser power reduction to 5 mW does not produce changes other than an intensity reduction in the Raman spectra, confirming that sample heating did

not affect our experiments. The scattered light was analyzed with a single spectrograph (Shamrock 303i) equipped with an edge filter and an air-cooled multichannel charge-coupled-device detector (iDus 420). The spectral resolution was better than 2 cm⁻¹. For PbCrO₄, Raman experiments were carried out by our group in the backscattering geometry using a Horiba Yvon Jobin LabRam spectrometer and were previously published.¹⁷ The results of those experiments have been included here for comparison with ab initio calculations and with the experiments performed in the other three compounds. For PbCrO₄, a 632 nm laser was used in the Raman experiments because of the high absorption of PbCrO₄ at 532 nm.

In the optical-absorption studies, we used for PbCrO₄ and SrCrO₄ 20- μ m-thick parallel face crystals, which were cleaved from the larger single crystals that we described above. For PbSeO₄ and SrSeO₄, 20- μ m-thick polycrystalline platelets were employed. The platelets were obtained by compressing a powder sample to 1 GPa using a large-volume press equipped with Bridgman anvils.²⁴ Optical-absorption measurements in the ultraviolet–visible–near-infrared (UV–vis–NIR) have been carried out by making use of both deuterium and halogen lamps integrated in the DH-2000 light-source from Ocean Optics. Light was collimated and focused on the samples by a confocal system consisting of a pair of Cassegrain reflecting objectives (15×). Transmittance of the samples was measured using the sample in/sample out method and detected with an Ocean Optics USB2000 UV–vis–NIR spectrometer.^{25–27} From it, we determined the absorption-coefficient spectrum and the energy of the fundamental band gap (E_g).

3. OVERVIEW OF THE CALCULATIONS

The ab initio simulations were performed with the Vienna Ab-initio Simulation Package (*VASP*)²⁸ program in the frame-work of density functional theory (DFT).²⁹ The atomic species were described with projected-augmented-wave pseudopotentials.³⁰ The exchange-correlation energy was taken in the generalized gradient approximation with the PBEsol prescription.³¹ Because of the presence of oxygen, a cutoff energy of 520 eV was used in order to obtain accurate results when calculating the valence electronic wave functions expanded in a plane-wave basis set. A dense Monkhorst-Pack³² special k-points grid was used for the Brillouin zone (BZ) integrations in all of our simulations. The k-points sampling and cutoff energy employed ensure a high convergence, better than 1 meV per formula unit, in the total energy. The optimized lattice external and internal parameters at different selected volumes were obtained for each compound by fully relaxing all of the internal atom positions and external lattice constants until the forces on the atoms were lower than 0.006 eV/Å and the stress tensor was diagonal, with differences smaller than 0.1 GPa (hydrostatic conditions). Our calculations provided a set of accurate energy (E), volume (V), and pressure (P) data for each compound, from which we obtained the crystal structure at ambient conditions and the P-V equation of state (EOS) for the studied compounds. The band structure and electronic density of states (DOS) are also calculated.

The direct method (direct force-constant approach)³³ was employed to study the lattice vibrations. The lattice-dynamic simulations of phonon modes were performed at the zone center (Γ point) of the BZ. The construction of the dynamical matrix at the Γ point required performing highly accurate calculations of the forces on the atoms when fixed small displacements from the equilibrium configuration of the atoms are considered. The number of needed independent displacements was reduced by using the crystal symmetry. Diagonalization of this matrix provided the frequencies of the modes, their symmetry, and their polarization vectors as well as the

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	351.9(3)	359.996	358.2(9)	358.8(5)	341.009	342.9(9)	342.1(5)	348.007	349.3(9)	348.4(3)
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Table 1. Unit-Cell Parameters and Volume Calculated for PbCrO₄, PbSeO₄, SrCrO₄, and SrSeO₄ Using DFT^a



Figure 1. (a) Energy–volume curves calculated for PbCrO₄, SrCrO₄, PbSeO₄, and SrSeO₄. In order to facilitate comparison, the energy curve of SeSeO₄ was shifted down by -43 eV, the energy curve of PbSeO₄ was shifted down by -23 eV, and the energy curve of PbCrO₄ was shifted down by -10 eV. (b) Unit-cell volume versus pressure for the four studied compounds.

irreducible representations and the character of the phonon modes at the Γ point. Temperature effects and zero-point energy have been included with the vibrational free energy calculated within the quasi-harmonic approximation.^{34–37} Finally, the supercell method was used to obtain the phonon dispersion, phonon density of states (PDOS), and projected DOS.

4. RESULTS

We will start describing the results of the XRD experiments. The structures of these compounds were accurately determined 3 decades ago by Effenberg and Pertlik,²¹ and we have confirmed that our samples have the monazite-type structure and determined the unit-cell parameters. These parameters are

given in Table 1. They agree within 0.5% with those reported in the literature. 21

We will now compare our structural calculations with the experimental results. We have made total energy calculations to determine the crystal structures of PbCrO₄, PbSeO₄, SrCrO₄, and SrSeO₄. The equilibrium unit-cell parameters were calculated by minimizing the crystal total energy obtained for different volumes. The atomic positions at the equilibrium volume were also calculated. Figure 1a shows the energy–volume curves for the four compounds. For the equilibrium volume, the calculated vibrational free energies in the quasi-harmonic approximation, at 300 K and including the zero-point energy, are 60.7, 78.5, 115.9, and 135.4 meV/pfu (per formula unit) for PbSeO₄, PbCrO₄, SrSeO₄, and SrCrO₄, respectively. The calculated unit-cell parameters are given in Table 1. The agreement with the experimental data is excellent. In Table 2,

Table 2. Calculated Atomic Positions for Monazite-Type PbCrO₄, PbSeO₄, SrCrO₄, and SrSeO₄^a

		PbCrO ₄	
Pb	0.2194 [0.22130]	0.1426 [0.14545]	0.4000 [0.39692]
Cr	0.2012 [0.20107]	0.1654 [0.16364]	0.8824 $[0.88184]$
O_1	0.2509 [0.2538]	0.0085 [0.0042]	0.0607 [0.0574]
O ₂	0.1244 [0.1245]	0.3464 [0.3425]	-0.0146 [-0.0110]
O ₃	0.0321 [0.0295]	0.0982 [0.0999]	0.6852 [0.6858]
O_4	0.3882 [0.3859]	0.2137 [0.2141]	0.7847 [0.7819]
		PbSeO ₄	
Pb	0.2157 [0.21598]	0.1479 [0.14932]	0.4053 [0.40191]
Se	0.1948 [0.19595]	0.1644 [0.16362]	0.8823 [0.88195]
O_1	0.2365 [0.2397]	0.0029 [0.0057]	0.0526 [0.0490]
O ₂	0.1163 [0.1196]	0.3440 [0.3396]	-0.0139 [-0.0142]
O ₃	0.0255 [0.0252]	0.1090 [0.1102]	0.6796 [0.6851]
O_4	0.3826 [0.3806]	0.2081 [0.2083]	0.7871 [0.7881]
		SrCrO ₄	
Sr	0.2269 [0.22813]	0.1574 [0.15869]	0.3980 [0.39806]
Cr	0.1974 [0.19769]	0.1651 [0.16487]	0.8860 [0.88691]
O_1	0.2583 [0.2584]	0.0033 [0.0055]	0.0597 [0.0562]
O ₂	0.1188 [0.1201]	0.3393 [0.3373]	0.0018 [0.0024]
O ₃	0.0231 [0.0256]	0.1002 [0.1012]	0.6917 [0.6981]
O_4	0.3798 [0.3776]	0.2214 [0.2179]	0.7848 [0.7881]
		SrSeO ₄	
Sr	0.2199 [0.22082]	0.1561 [0.15773]	0.4005 [0.39876]
Se	0.1931 [0.19364]	0.1647 [0.16510]	0.8857 [0.88588]
O ₁	0.2467 [0.2484]	0.0029 [0.0052]	0.0592 [0.0552]
O ₂	0.1125 [0.1154]	0.3392 [0.3375]	0.0000 [-0.0004]
O ₃	0.0178 [0.0192]	0.1049 [0.1094]	0.6868 [0.6935]
O_4	0.3774 [0.3752]	0.2154 [0.2167]	0.7859 [0.7872]
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"All atoms are at 4e Wyckoff positions. The experimental positions²¹ are also included in square brackets for comparison.

we present the calculated atomic positions and compare them with those obtained from single-crystal XRD.²¹ The agreement between the calculations and experimental results is again excellent. Both facts indicate that DFT calculations accurately describe the crystal structures of the four studied compounds, suggesting that DFT could be a powerful tool to calculate other physical properties of PbCrO₄, PbSeO₄, SrCrO₄, and SrSeO₄. In particular, from the energy–volume curves shown in Figure 1a, we obtained the pressure dependence of the unit-cell volume. The results we obtained are shown in Figure 1b. It can be seen that the four compounds have similar compressibilities, with PbCrO₄ being the most compressible compound among them. We also fitted the energy–volume curves with a Birch– Murnaghan third-order EOS^{38} to determine the bulk modulus and its pressure derivative, two important parameters that characterized the behavior of the materials under compression. These parameters are given in Table 3. For PbCrO₄, the

Table 3. Unit-Cell Volume (V_0) , Bulk Modulus (B_0) , and Its Pressure Derivative (B'_0) Determined Using a Third-Order Birch-Murnaghan EOS To Fit the DFT Results of Figure 1

	V_0 (Å ³)	B_0 (GPa)	$B_0{}'$
PbCrO ₄	348	51.89	4.92
PbSeO ₄	360	56.75	4.56
SrCrO ₄	341	58.70	4.58
$SrSeO_4$	348	57.83	5.08

theoretical bulk modulus (51.89 GPa) is comparable with the experimental value (56 \pm 1 GPa),² which was determined with a second-order Birch–Murnaghan EOS. In our case, if the second-order EOS is used in the fitting of the energy–volume curves, the bulk modulus is 53.84 GPa. For the other three compounds, there are no previous results to compare them with. According to our calculations, PbCrO₄ (PbSeO₄) is more compressible than SrCrO₄ (SrSeO₄), which is consistent with the behavior observed when PbMoO₄ (PbWO₄)^{39,40} is compared with SrMoO₄ (SrWO₄).^{41,42}

We will now discuss the vibrational properties of the studied materials. From factor group analysis, it can be established that the monazite structure presents 36 Raman-active phonons ($\Gamma = 18B_g + 18A_g$), 33 IR-active phonons ($\Gamma = 16B_u + 17A_u$), and three acoustic phonons ($\Gamma = 2B_u + 1A_u$) at the zone center. The Raman- and IR-active modes have been reported earlier for



Figure 2. Raman spectra of the four studied compounds. The low-frequency region is magnified $(5\times)$ to better show the modes of this region, which are the least intense modes.

Table 4. Experimental	(expt) and Calculated	(theory) Raman Modes	of All Monazite Co	ompounds (cm ⁻¹)	Including Mode
Assignment					

	PbSeO ₄			$SrSeO_4$			$SrCrO_4$			PbCrO ₄	
mode	theory	expt	mode	theory	expt	mode	theory	expt	mode	theory	expt
Ag	46.70	46	Bg	60.04	60	Bg	58.37		Ag	43.83	42
Bg	47.40		Ag	69.25		Ag	64.81		Bg	44.60	45
Ag	48.93		Ag	76.39		Ag	76.62	79	Ag	49.83	
Bg	58.41	59	Bg	84.59	84	Ag	91.66	89	Bg	52.40	57
Ag	61.31		Ag	93.40		Bg	92.16	94	Ag	54.77	62
Bg	66.25	66	Bg	104.47	104	Bg	106.61	108	Bg	61.98	73
Ag	79.09	79	Bg	109.28	109	Ag	109.68		Bg	81.80	81
Bg	81.59		Ag	112.34		Bg	114.38	114	Ag	85.13	83
Ag	94.80		Bg	117.62	117	Bg	119.42		Ag	99.87	95
Ag	99.34	100	Ag	126.42	126	Ag	122.69	127	Ag	104.41	99
Bg	107.34		Ag	127.52		Ag	130.29	138	Bg	110.41	110
B_g	108.51	111	Bg	144.30	144	Bg	155.04		Bg	121.75	116
Bg	125.69	125	Ag	148.74	148	Ag	158.74	161	Ag	137.56	136
Ag	129.96		Bg	167.08	167	Bg	174.72	177	Bg	145.27	149
Bg	135.20	134	Bg	168.75		Bg	184.36	181	Bg	146.77	
Ag	155.11	156	Ag	188.40	180	Bg	192.13	187	Ag	158.08	178
Bg	182.56	171	Bg	197.14	195	Ag	192.40	196	Bg	184.43	185
Ag	191.53	188	A _g	204.84		A _g	197.40	211	A _g	185.00	
Bg	285.40		Bg	295.44	311	Bg	333.60	333	Bg	321.76	327
Ag	297.17	315	Å	308.91	328	Å	344.17	342	Å	335.13	338
Ag	327.90	328	Ag	347.31	341	Bg	349.04	350	Bg	346.51	347
Bg	353.24	358	Å	365.22	365	Å	359.88	364	Å	346.67	359
Ag	356.05	387	Bg	376.69	377	Ag	367.12	367	Ag	353.71	378
Ag	371.69	405	Ăg	391.74	397	Bg	389.44	376	Bg	369.96	402
Bg	379.50	413	Bg	391.74	427	Åg	391.84	398	Ăg	367.00	407
Bg	389.44	425	Bg	411.72	448	Bg	399.24	403	Bg	375.39	440
Ag	399.64	430	Ăg	434.30	463	Bg	423.16	424	Bg	393.97	451
Bg	408.35	437	Bg	440.20	467	A _g	429.10	432	A _g	394.21	479
Ag	774.34		A _g	814.50		Bg	901.39	859	A _g	866.83	801
Ag	791.28	821	Bg	821.04	854	Ag	904.16	868	Ag	877.64	825
Bg	791.85	827	Ag	830.14	871	Ag	910.20		Bg	879.78	
Ăg	808.23	832	Ăg	838.45	884	Ăg	933.91	894	Ăg	886.35	840
Bg	808.29	837	Bg	845.89	889	Bg	938.72	918	Bg	894.32	
Bg	809.79	846	Ăg	858.76	900	Ăg	941.05	932	Ăg	906.46	856
Å	821.44	860	Bg	866.27	908	Bg	959.73	951	Bg	914.63	879
Bg	826.41	863	Bg	870.40	916	B _g	975.61	970	B _g	922.74	

PbCrO₄, PbSeO₄, SrCrO₄, and SrSeO₄.^{43,44} However, less than half of the expected Raman and IR modes have been measured.43,44 In contrast, for the case of PbCrO4, our recent Raman measurements,¹⁷ performed using state-of-the-art techniques, found 30 Raman-active modes. Here we report new Raman experiments for PbSeO₄, SrCrO₄, and SrSeO₄. These results, together with those we previously reported for PbCrO₄, will be compared here with previous studies^{43,44} and our ab initio calculations. Figure 2 shows the Raman spectra of the four compounds. All of the studied compounds do not have Raman-active modes from 500 to 800 cm⁻¹. The Raman modes in the low-wavenumber region are weaker than the modes in the high-wavenumber region. For these reasons, we introduced in the plot a break in the horizontal axis and magnified 5 times the Raman spectra in the low-wavenumber region to facilitate identification of the Raman modes on it. The first conclusion we obtained from the figure is that the four compounds have a similar overall mode distribution. Ticks in the figure show the identified Raman modes. A total of 30 modes have been

detected for PbCrO₄ and SrCrO₄ and 28 modes for PbSeO₄ and SrSeO4. A Lorentzian multipeak fitting analysis was used to identify partially overlapping peaks.⁴⁵ The wavenumbers determined for the observed Raman modes are summarized in Table 4. In those cases, a comparison with the literature^{43,44} is possible and the agreement is quite good. Table 4 also gives the theoretically calculated wavenumbers. Calculations also allowed us to make a mode assignment, which is given in the table. It can be seen that the agreement between theory and experiments is excellent in the low-frequency region (below 205 cm⁻¹). For the rest of the Raman modes, theory and experiments agree within 10%. This small discrepancy between the DFT calculations and experiments has previously been observed in related compounds.^{9,46} In particular, in the highfrequency region (above 750 cm^{-1}), the wavenumbers are underestimated by calculations in selenates and overestimated in chromates; see Table 4.

The crystal structure of monazite has been broadly discussed in the literature. $^{\rm 47}$ In our case, it can be viewed as being

Table 5. Experimental (expt)^{32,33} and Calculated (theory) IR Modes of All Monazite Compounds (in cm⁻¹) Including Mode Assignment

	PbSeO ₄			$SrSeO_4$			$SrCrO_4$			PbCrO ₄	
mode	theory	expt	mode	theory	expt	mode	theory	expt	mode	theory	expt
A _u	50.80		A _u	75.89		A _u	74.48		A _u	48.53	
B_u	56.37		B _u	78.29		B_u	82.19		A_u	55.77	
A_u	58.81		A _u	98.63		A _u	100.84		B_u	55.84	
B _u	74.85		B_u	107.81		A _u	102.97		A_u	75.52	
A_u	81.36		A _u	111.01		B_u	114.75		B_u	77.89	
A_u	87.13		B _u	119.18		B_u	129.86		B _u	90.33	
B_u	93.23		A _u	129.49		A _u	131.69		A _u	99.90	
B_u	103.07		A _u	143.07		A _u	140.50		A _u	114.91	
A_u	106.47		B_u	148.70		B_u	146.30		B_u	117.21	
B_u	108.44		B_u	149.90		B_u	152.71		B_u	121.18	
A_u	133.09		A _u	172.39		A _u	159.98		A _u	132.66	
B _u	145.33		A _u	176.82		B _u	185.39		A _u	154.11	
A_u	154.87		B_u	180.02		A _u	188.63		B_u	157.18	
A_u	170.98		A _u	194.33		A _u	200.64		A _u	167.98	
B_u	178.62		B _u	208.44		B _u	210.78		B _u	177.46	
A _u	276.59		B _u	288.83		B _u	324.89		B _u	314.22	
B_u	279.93		A _u	290.27		A _u	331.90		A _u	318.92	
A_u	332.06		A _u	343.40		A _u	339.13		A _u	335.37	
B_u	343.90		B_u	365.22		B_u	367.92	350	B_u	344.37	
A_u	359.72		A _u	376.83		A _u	375.89		A _u	351.38	
B _u	363.75	366	B _u	380.43	381	A _u	379.16		A _u	362.42	
A _u	380.23	372	A _u	399.84	396	B_u	383.30		B _u	371.22	
B _u	382.63	394	B _u	400.38	414	B_u	397.54		B _u	379.33	
B _u	396.84	415	B _u	421.26	425	B _u	423.86	410	B _u	390.37	397
A _u	407.11	427	A _u	443.87	447	A _u	441.91	431	A _u	415.45	
B _u	769.53		B _u	806.02		B _u	888.11	845	B _u	860.13	833
A_u	773.87		A _u	806.06		A _u	892.32	855	A_u	871.00	858
B _u	785.18		B_u	829.31		A _u	914.57	875	B_u	876.04	
A_u	790.18		A_u	829.37	844	B_u	916.93	887	A_u	878.74	
A_u	807.89		B _u	841.92	867	B_u	934.55	912	B _u	885.25	
B _u	807.89	820	A_u	846.35	884	A _u	946.45	927	A_u	893.75	
B _u	831.31	827	B _u	871.90	904	B_u	960.03		B _u	924.81	905
A _u	835.98	857	A _u	877.61	919	A _u	969.44		A _u	929.18	

composed of [001] chains formed of alternating polyhedral SrO_9 (PbO₉) and SeO₄ (CrO₄) tetrahedral units. Therefore, to a good approximation, the monazite structure can be considered as composed of two alternating sublattices separately containing the Sr (Pb) and SeO₄ (CrO₄) ions. As a consequence, the vibrational spectra of monazites have been interpreted in terms of internal modes associated with the SeO₄ (CrO_4) tetrahedron,⁴⁸ in which the center of mass of the SeO₄ (CrO_4) units does not move, or external modes, when they involve movements of both the Sr (Pb) and SeO_4 (CrO₄) ions. The external modes can be divided into translational- and rotational-like modes, and the internal modes can be classified as bending and stretching modes. In general, the external modes occur at low wavenumber.48 In addition, the internal stretching modes are the most intense modes and occur at the highest frequencies.

According to our calculations, we tentatively assigned the external and internal modes of the four studied compounds. They are separated by extra rows of space in Table 4. The modes on the top of the table are the external modes (wave-numbers between 0 and 210 cm^{-1}). The modes in the center of the table are the internal bending modes (wavenumbers

between 300 and 475 cm⁻¹), and the modes in the bottom of the table are the internal stretching modes (wavenumbers between 750 and 1000 cm⁻¹). As expected, the last modes are the most intense modes in our experiments; see Figure 2. In particular, the most intense mode is the symmetric stretching $A_g \mod^{43,44,48}$ usually named as $\nu_1(A_g)$. In our experiments, the most intense modes are located at 840 cm⁻¹ in PbCrO₄, 846 cm⁻¹ in PbSeO₄, 868–894 cm⁻¹ in SrCrO₄, and 871 cm⁻ in SrSeO₄, suggesting that these are the symmetric stretching A_g modes of the four compounds. Previously, Scheuermann et al.43,44 tentatively made the same mode assignment in PbCrO₄ and PbSeO₄. On the other hand, these authors proposed the mode at 860-868 cm⁻¹ in SrCrO₄ and 854- 870 cm^{-1} in SrSeO₄ as the symmetric stretching A_g mode. In SrSeO₄, the second mode agrees with our suggestion for this. In $SrCrO_4$, the mode at 868 cm⁻¹ proposed by Scheuermann et al. agrees with one of our candidates for the $\nu_1(A_{\sigma})$ mode. Note that the frequency of this mode is slightly different in monazitetype PbCrO₄ (840 cm⁻¹), SrCrO₄ (868 cm⁻¹), and LaCrO₄ (830 cm⁻¹), 49 which implies that the mode frequency is slightly sensitive to a change of the nine-coordinated cation (Sr, Cr, and La). However, the frequency difference from one



Figure 3. PDOSs of (a) PbCrO₄, (b) SrCrO₄, (c) PbSeO₄, and (d) SrSeO₄.

compound to the other is around 3%, while the frequency difference between the external modes of $SrCrO_4$ and $PbCrO_4$ range from 6% to 50%. These facts justify the use of the internal/external mode model as a first approximation to describe lattice vibrations in monazites.

It is also interesting to note here than in other chromates, where Cr is in tetrahedral coordination, that the symmetric stretching A_g mode is also always the most intense Ramanactive mode, having frequencies similar to those observed in monazite-type chromates, e.g., BaCrO₄ (862 cm⁻¹),⁵⁰ YCrO₄ (863 cm⁻¹),⁵¹ Ag₂CrO₄ (847 cm⁻¹),⁵² CaCrO₄ (880 cm⁻¹),⁵³ and NdCrO₄ (844 cm⁻¹).⁴⁹ This fact is not a mere coincidence but a consequence of the fact that the mode frequency is basically determined by the Cr–O bond strength, which should be similar in all chromates discussed here because in all of them Cr is identically coordinated and the Cr–O distances are similar.⁵⁴ This is consistent with the fact that the frequency of the $\nu_1(A_r)$ mode decreases following the sequence SrCrO₄

 $(868 \text{ cm}^{-1}) > \text{PbCrO}_4 (840 \text{ cm}^{-1}) > \text{LaCrO}_4 (830 \text{ cm}^{-1}) \text{ and}$ the Cr–O average bond distance increases following the sequence SrCrO₄ (1.626 Å) > PbCrO₄ (1.663 Å) > LaCrO₄ (1.703 Å).

There are in the literature many empirical rules relating the Raman stretching frequencies to the bond length.⁵⁵ One of these is Badger's rule,⁵⁵ which has been found not to adequately correlate bond distances to stretching frequencies in chromates.⁵⁶ A more accurate relationship for chromates was developed by Weckhuysen and Wachs.⁵⁶ They proposed the following expression for the bond length–stretching frequency correlation:

$$v_1 = 13055 \exp(-1.6419R)$$

where ν_1 is in cm⁻¹ and the Cr–O bond distance, *R*, in Å. Using this expression, we obtained $\nu_1 = 851$ (886) cm⁻¹ for PbCrO₄ (SrCrO₄). These values differ by less than 2% from the wavenumbers that we determined experimentally, which

support the assignation that we made for the symmetric stretching mode.

To conclude the discussion on Raman modes, we would remark that, among the stretching modes, there should be $4 A_g$ and $4 B_g$ modes, which is in agreement with our mode assignment (see Table 4). In addition, among the bending modes, there should be $6 A_g$ and $6 B_g$ modes, which have been properly identified in Table 4. Finally, we assigned 9 A_g and 9 B_g external modes for each compound as expected.

From our DFT calculations, we have also determined the IR-active frequencies for the four studied compounds. To the best of our knowledge, the only previous study of IR modes was made by Scheuermann et al.^{43,44} more than 40 years ago. In their works, between 4 and 10 modes were reported for the different compounds. They are summarized in Table 5. In the table, we also report the calculated frequencies for the 33 IR-active modes, together with their mode assignment. Again, the modes can be divided into external (13 modes), internal bending (10 modes), and internal stretching (8 modes). The three types of modes are separated by dotted lines in the table, going from external modes in the top (low-wavenumber region), to internal bending in the center (central-wavenumber region), and internal stretching in the bottom (high-wavenumber region). The IR mode distribution in frequencies is qualitatively similar to the Raman mode distribution. The information obtained from our calculations and summarized in Table 5 will allow mode assignment in future experiments. As can be seen in the table, the agreement between the calculated and measured IR modes is as good as that for the Raman modes. Therefore, our calculations can be a good guide in future IR measurements. Note that previous studies did not report any of the external IR modes.

To conclude the discussion of lattice vibrations, we would comment that, in addition to phonon frequencies at the Γ point, we have also calculated the PDOSs for the four compounds, which are given in Figure 3. As can be seen, in the harmonic approximation, there are no imaginary phonon branches near the Γ point; therefore, the monazite phase is dynamically stable. In general, the PDOSs of the four compounds present three zones separated by two phonon gaps: one around $\approx 200-300$ cm⁻¹ and another larger one between ≈ 400 and ≈ 800 cm⁻¹. According to the PDOS, it is observed that in the low-frequency zone the PDOS is composed of vibrations of PbO₉ (SrO₉) polyhedra and a lower contribution by CrO_4 (SeO₄) tetrahedra. The intermediate-frequency zone is mainly due to vibrations from the tetrahedron with a very small contribution from the PbO_o (SrO_9) polyhedra, while the high-frequency zone is only due to vibrations from CrO_4 (SeO₄). In this sense, the vibrational spectra of the four studied compounds can be interpreted in terms of modes from the CrO_4 (SeO₄) tetrahedra, which can be considered as independent units in the monazite structure. Thus, our calculations confirm that the phonon modes in the studied monazites can be classified either as internal (the CrO₄ or SeO₄ center of mass does not move) or as external (movements of CrO_4 or SeO_4 tetrahedra as rigid units).

We will now describe the results of the optical-absorption studies. The absorption coefficient (α) of the four studied compounds at ambient conditions is shown in Figure 4 (top). The absorption spectrum shows a steep absorption, which corresponds to the fundamental absorption plus a low-energy absorption band that overlaps partially with the fundamental absorption. The low-energy absorption band has been



Figure 4. (Top) Measured absorption spectra (solid lines) and fits (dotted lines). (Bottom) Tauc plots used to determine E_g . The dashed lines show extrapolation of the linear region to the abscissa.

Table 6. Experimental and Theoretical Values of the Band Gaps (E_g) at Ambient Pressure

	expe	riment	theory				
compound	$E_{\rm g}~({\rm eV})$	$E_{\rm u}~({\rm eV})$	E _g (e	V)			
PbCrO ₄	2.25(5)	0.066(6)	$A-Y \rightarrow Y: 1.6183$	$Y \rightarrow Y: 1.7153$			
$SrCrO_4$	2.45(5)	0.083(8)	$Y \rightarrow Z-\Gamma$: 2.6762	$Y \rightarrow \Gamma$: 2.6860			
PbSeO ₄	4.30(5)	0.090(9)	$Y \rightarrow C: 3.1798$	$C \rightarrow C: 3.2832$			
$SrSeO_4$	4.75(5)	0.094(9)	$Y \rightarrow \Gamma$: 3.6182	$\Gamma \rightarrow \Gamma$: 3.6292			

"The Urbach energy (E_u) determined from the fits to the experimental results is also included. For the calculations, we have listed the k points for the top of the valence band and bottom of the conduction band.

previously observed in related ternary oxides and seems to be related to the presence of defects.^{17,26,27} Its nature has been the subject of considerable debate⁵⁷ and is beyond the scope of this work. This tail overlaps partially with the fundamental absorption, which makes it hard to conclude whether the smallest band gap is direct or indirect. In previous works, on the basis of the large values measured for the absorption coefficient of PbCrO₄, it was assumed that this material was a direct-bandgap material, determining that E_g was 2.3 eV.^{6,17} However, the gradual increase of α (with respect to the photon energy) that we observed in the four studied compounds suggests an indirect nature for the fundamental band gap. Therefore, to determine more accurately the nature of the fundamental band gap, we analyzed the experimental results using a Tauc plot.⁵⁸ We found that for high energies $(\alpha h \nu)^{1/2}$ is proportional to the

SrCrO₄ PbCrO. (a) (b) 34 2 1. 1. (eV) Energy (eV) Energy (0.4 0 -0.4 -0.4 -1.3 -1.: SrSeO PbSeO (d) (c) 4. 3 3 Energy (eV) Energy (eV) 2. 0.4 n -0.4 0. 1. -1.:

Figure 5. Band structures of (a) PbCrO4, (b) SrCrO4, (c) PbSeO4, and (d) SrSeO4.

photon energy $(h\nu)$, as can be seen in Figure 4 (bottom), which supports the hypothesis that the four materials are indirect-band-gap semiconductors. This conclusion is in good agreement with our band-structure calculations. From the Tauc plots shown in Figure 4, we estimated E_g for the four compounds by extrapolating the linear region of $(\alpha h\nu)^{1/2}$ to the abscissa (blue dashed lines). The obtained values are summarized in Table 6. The value determined here for PbCrO₄ [$E_g = 2.25(5)$ eV] is slightly smaller but consistent with the value that we determined previously ($E_g = 2.3$ eV). The band gap determined for SrCrO₄ [$E_g = 2.44(5)$ eV], ¹⁴ suggesting that other studies overestimate the value of E_g^{-13-15}

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In contrast with the chromates, which absorb visible light, we found that the selenates only absorb UV light and have band gaps more than 2 eV larger than those in their chromate counterpart. In addition, in Table 6, it can be seen that the Pb compounds have a smaller E_g than the Sr compounds, which is consistent with the observations when PbWO₄ (PbMoO₄) is compared with SrWO₄ (SrMoO₄).⁵⁹ The reasons for this behavior will be discussed when the results of the electronic structure calculations are described. Before going into this discussion, we would mention that the measured absorption spectra can be well fitted assuming that the low-energy part of the absorption edges exhibits an exponential dependence on the photon energy following Urbach's law⁶⁰ and that the high-energy part can be described by an allowed indirect transition. Under this assumption and when the phonon

absorption and emission are neglected, the absorption spectrum is given by

$$\alpha(h\nu) = \begin{cases} A_{1} e^{(h\nu - E_{g})/E_{u}}, & h\nu \leq E_{g} + 2E_{u} \\ A_{2}(h\nu - E_{g})^{2}, & h\nu \geq E_{g} + 2E_{u} \end{cases}$$

where the parameters A_1 and A_2 are correlated by imposing that $\alpha(h\nu)$ should be continuously differentiable. This condition also determines the $E_g + 2E_u$ critical energy, below which the Urbach exponential absorption is assumed, where E_u is the Urbach energy. Assuming the E_g values determined from the Tauc plots (see Table 6) and using an iterative procedure, we have fitted the absorption spectra shown in Figure 4 (top). The fits (red dotted lines) reproduce well the experimental results (black solid lines), indicating that assuming an indirect band gap plus an Urbach tail is a reasonable hypothesis to describe the absorption spectra of the four studied compounds. From the fits, we have determined E_u , which is also related to the steepness of the absorption tail. The values obtained are summarized in Table 6. They are comparable with the values obtained in related ternary oxides.^{17,26}

We will now discuss the results of the electronic structure calculations. The calculated band structures and DOSs of the four studied compounds are shown in Figures 5 and 6, respectively. The band structures are qualitatively similar in all cases. According to calculations, $PbCrO_4$, $PbSeO_4$, $SrCrO_4$, and $SrSeO_4$ are indirect-band-gap materials. This fact is in

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Figure 6. Total and partial DOSs of (a) PbCrO₄, (b) SrCrO₄, (c) PbSeO₄, and (d) SrSeO₄.

agreement with the conclusion extracted from the Tauc plot analysis. The calculated band-gap values are summarized in Table 6. These values underestimated the experimental values by around 1 eV (0.6 eV) in the selenates (PbCrO₄). In the case of SrCrO₄, theory slightly overestimates the band-gap energy (see Table 6). These discrepancies are typical of DFT calculations.^{26,27} In spite of that, the calculated ordering of the band gaps is given by PbCrO₄ < SrCrO₄ < PbSeO₄ < SrSeO₄, which is in agreement with the experiments.

Let us describe now in detail the band structures of the different compounds (Figure 5). One important feature of the band structures is that, with the exception of PbCrO₄, the dispersion of the valence bands is relatively small, with comparable dispersions along different directions. In PbCrO₄, the maximum of the valence band is between the Y and A points of the BZ and the minimum of the conduction band at the Y point. Calculations also established that the Y-Y direct band gap is 0.1 eV higher than the indirect band gap. In SrCrO₄, the maximum of the valence band is the Y point of the BZ. On the other hand, the conduction band has two minima very close in energy, one at the Γ point of the BZ and the other between the Z and Γ points. Consequently, SrCrO₄ has two indirect band gaps that are separated by only 0.01 eV, as shown in Table 6. In PbSeO₄, there are two maxima in the valence band at the Y and C points of the BZ, separated by 0.1 eV. Additionally, the minimum of the conduction band is also at the C point of the BZ. Consequently, PbSeO₄ has an indirect band gap of 3.17 eV and a direct band gap of 3.28 eV. In the fourth compound, SrSeO₄, there are two maxima in the valence

band separated by 0.01 eV, at the Y and Γ points of the BZ. In this material, the minimum of the conduction band is at the Γ point of the BZ. Consequently, SrSeO₄ has an indirect band gap and a direct band gap, which are nearly degenerated.

We will discuss now the nature and relative magnitude of the band gaps of the different studied compounds. In order to do this, we will use the calculated DOSs given in Figure 6. It can be seen that, in the four compounds, the upper part of the valence band is dominated by O 2p states. On the contrary, the lower part of the conduction band is composed primarily of electronic states associated with the Cr 3d (Se 4s) and O 2p states. Therefore, as a first approximation, it can be considered that the band-gap energy of the chromates and selenates is mainly determined by the molecular electronic structure of the CrO₄²⁻ and SeO_4^{2-} ions in which the hexavalent atom is in a tetrahedral environment. The classical field splitting in the SeO_4^{2-} ion is much larger than that in CrO_4^{2-} ion, which strongly supports our previous statement. Additional support to our conclusion comes from the fact that different related ternary oxides containing Pb (and having related crystal structures) have band gaps ordered following the sequence $PbCrO_4 < PbMoO_4 < PbWO_4 < PbSeO_4$. That is, the band gap increases as the field splitting increases: $CrO_4^{2-} < MoO_4^{2-} <$ $WO_4^{2-} < SeO_4^{2-}$. Another important fact that can be seen in Figure 6 is that the Sr states are completely empty near the Fermi level. Thus, they do not have any influence on the bandgap energy. On the contrary, in PbCrO₄ and PbSeO₄, there is a contribution of Pb 6s electrons to the top of the valence band and of Pb 6p states to the bottom of the conduction band.

As a consequence, the band gap is smaller in the Pb compounds than in the Sr compounds, as we found in the experiments. Notice that the same conclusion can be extracted from the comparison of the band gaps of $PbWO_4$ ($PbMoO_4$) and $SrWO_4$ ($SrMoO_4$).⁵⁹

5. CONCLUDING REMARKS

We performed an experimental and theoretical study of PbCrO₄, SrCrO₄, PbSeO₄, and SrSeO₄ that has allowed us to analyze the structural, electronic, and vibrational properties of the four compounds. We found that calculations accurately reproduce the crystal structure of the four materials. They also are useful to deepen the understanding of the electronic and vibrational properties. In particular, calculations have helped us with the assignment of phonon modes and allowed us to predict where future experiments might find the as-yetunobserved IR-active modes. Finally, the study of the electronic structure has demonstrated that the studied chromates and selenates behave as indirect-band-gap materials, with the chromates having a band gap in the visible and the selenates a band gap in the UV. Using theoretical calculations, we have been able to propose an explanation to this fact and also understand why the Pb compounds have a smaller band gap than the Sr counterparts.

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Notes

The authors declare no competing financial interest.

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