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PHYSICAL METHODS OF INVESTIGATION

Low-Frequency Raman Lines as an Indicator of the Presence of Lead in Oxide Materials

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Abstract—Raman spectra were obtained for single- and polycrystalline specimens of some oxide compounds used as quantum electronic materials and for native minerals containing complex anions, where the cations are alkaline-earth metals and lead. An analysis of the low-frequency regions of the Raman spectra showed that, in some cases, the pair of high-intensity lines appearing in the range below 100 cm^{-1} serves as an indicator of the presence of Pb^{2+} ions.

Keywords: Raman spectroscopy, sulfates, celestite, barite, anglesite, carbonates, strontianite, viterite, cerussite, phosgenite, molybdates, tungstates, scheelite, lead

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INTRODUCTION

Raman spectroscopy is an informative and convenient nondestructive identification method. Now Raman spectroscopy is applied in the fields such as gemology, archeology [1], and even agriculture [2]. In some cases, Raman spectra serve to elucidate the chemical bonding specifics in compounds.

Our goal in this study was to elucidate the trends in Raman spectra of lead-containing inorganic compounds as compared to their analogues containing alkaline-earth ions.

EXPERIMENTAL

The subject matters of our study were minerals from native deposits (borrowed from the collection of the Fersman Mineralogical Museum) and tungstate and molybdate single crystals usable as lasing materials [3, 4] (Table 1).

The Raman spectra were excited by an ILA-120 argon laser in a continuous mode (λ = 488.0 and 514.5 nm) or by a copper vapor laser in a quasi-continuous mode with the repetition frequency 15 kHz (510.6 and 578.2 nm). The average radiation power in both cases was about 1 W. The back-scattering geometry was used. Back-scattering spectra were recorded with a SPEX-Ramalog 1403 double monochromator. A PMT signal was transduced to a computer to be further processed. The instrumental resolution was ~1 cm^{-1}.

All of our native mineral specimens having natural grain orientation, the Raman spectra obtained in the experiment were partially polarized. The scheelite specimens were oriented, and the spectra were recorded for two positions: (1) with the polarization plane of the incident beam parallel to the optical axis that coincided with crystallographic axis c_4; and (2) for the case where the optical axis was normal to the polarization axis of the incident laser beam.

RESULTS AND DISCUSSION

All subject matters of the study are oxide materials. In this type of compound, X-ray structural analysis identifies oxygen-containing anions shaped either as planar triangles ($[CO_3]^{2-}$) or as isometric tetrahedra ($[SO_4]^{2-}$, $[WO_4]^{2-}$, and $[MoO_4]^{2-}$). The bonding between the complex-forming atom and the surrounding oxygen atoms is stronger than between oxygen and the outer-sphere cation. In this case, the nearly-free-anion approximation is applied, and two regions are recognized in the vibrational spectrum, namely, the region where internal vibrations appear (the vibrational motions of the constituent atoms of the anions relative to one another appearing in a high-frequency spectral range) and the region where external (lattice) vibrations appear (the motion of complex anions as a whole relative to the cation sublattice) [5]. The description of relative atomic displacements upon internal vibrations in a planar triangular anion $[XO_3]$ may be found in [5], and the same for tetrahedral $[XO_4]$, in [6]. When the chemical bonding of outer-sphere cations to oxygen is quite strong, however, a

Table 1. Native mineral specimens (indexed to correspond with their numbering in the systematic collection of the Fersman Mineralogical Museum) and artificially grown single crystals of scheelite tungstates and molybdates

Cation	Anion				
	native minerals			Single crystals of scheelite $CaWO_4$ structure type	
	$[Cl_2CO_3]^{2-}$	Aragonite ($CaCO_3$) structure type	Barite $BaSO_4$ structure type		
		$[CO_3]^{2-}$	$[SO_4]^{2-}$	$[WO_4]^{2-}$	$[MoO_4]^{2-}$
Sr^{2+}	–	Strontianite[2]	Celestite[5]	+	+
Ba^{2+}	–	Viterite[3]	Barite[6]	+	+
Pb^{2+}	Phosgenite[1]	Cerussite[4]	Anglesite[7]	+	+

[1] No. 49061: from the oxidation zone of the Tsumeb polymetallic mine, Namibia.
[2] No. 12678: from the strontianite mine near Drensteinfurth, North Rhine-Westphalia, Germany.
[3] No. 33322: from the Arpaklen barite–viterite mine, Kopetdag, Turkmenistan.
[4] No. 5999: from the oxidation zone of the lead–silver deposit, Trekhsvyatskii mine, Nerchinsk area, East Transbaikalia.
[5] No. 74250: from sedimentary rocks of the Vodinskoe sulfur deposit, the Volga region (the Raman spectrum of specimen No. 34796: from sedimentary rocks near the village of Priluk, Pinega River, Arkhangelsk oblast, has a completely identical pattern).
[6] No. 74709: from hydrothermal veins near Cote d'Abot, Saint-Saturnin, Auvergne, France.
[7] No. 57700: from the oxidation zone of the Blyava polymetallic deposit, South Urals.

complex anion ceases to be "free" and the Raman spectral pattern becomes distorted.

The Spectra of Phosgenite and Aragonite Family Minerals

Figure 1 shows Raman spectra for aragonite family minerals and phosgenite. The spectra feature well-defined internal vibrations in the carbonate anion (at frequencies above 500 cm^{-1}) and external vibrations, what we call lattice vibrations. The full-symmetry vibration $\nu_1(A'_1)$ in the range ~1050–1085 cm^{-1}, vibrations $\nu_3(E')$ at ~680–705 cm^{-1} and $\nu_4(E')$ at ~1350–1400 cm^{-1} constitute the set of internal vibrations in the $[CO_3]^{2-}$ ion. It is noteworthy that a pair of very strong lines (whose intensities are commensurate to the values of full-symmetry internal vibrations in $[CO_3]^{2-}$) is observable at 58 and 71 cm^{-1} in phosgenite and cerussite spectra.

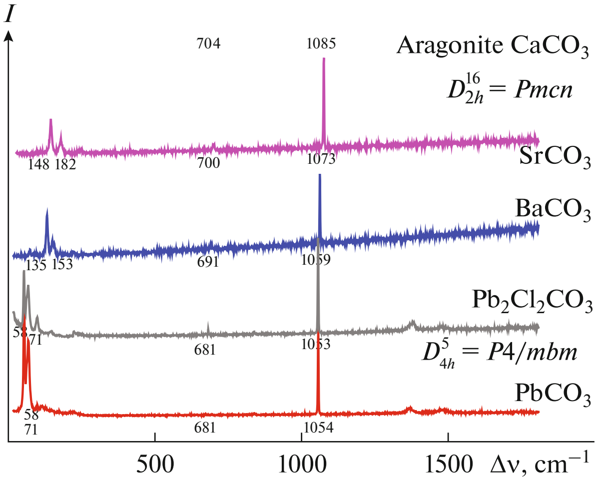

Fig. 1. Unpolarized Raman spectra of phosgenite and aragonite family carbonates in the range 0–1800 cm^{-1}. The figures denote the characteristic frequencies of lattice vibrations.

The Spectra of Barite Family Crystals

Figure 2 shows the Raman spectra of barite family minerals. The spectra of this type, just as those of the aragonite minerals, feature well-defined ranges of internal vibrations of the tetrahedral sulfate ion and the range where external vibrations appear. The full-symmetry vibration $\nu_1(A_1)$ at ~1000 cm^{-1}, vibrations $\nu_3(F_2)$ at ~1150 cm^{-1} and $\nu_2(E)$ at ~450 cm^{-1}, and a set of lines due to vibration $\nu_4(F_2)$ at ~620 cm^{-1}, constitute the set of $[SO_4]^{2-}$ internal vibrations. Noteworthy, weak external lattice vibrations are almost unobservable. This is due both to the polycrystallinity of the test samples and to the samples being colored and absorbing in the wavelength range of the exciting laser beam.

The Spectra of Scheelite Family Crystals

Figures 3 and 4 show polarized Raman spectra (more exactly, their fragments up to 400 cm^{-1}) in tungstate and molybdate scheelite crystals, respectively. Voron'ko et al. in their works, see, e.g., [7], considered the ranges of internal vibrations in $[WO_4]^{2-}$ ($[MoO_4]^{2-}$) tetrahedral anions and the ranges of external vibrations. Our study focuses on the range of external lattice vibrations. From Figs. 3 and 4 (HV polariza-

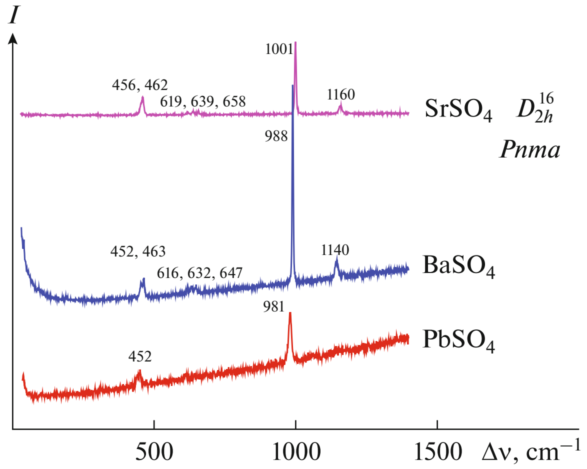

Fig. 2. Unpolarized Raman spectra of barite family sulfates in the range 0–1400 cm^{-1}. The figures denote the characteristic frequencies of lattice vibrations.

tion), one can see that strong lines appear in the range of frequencies below 100 cm^{-1} for lead tungstate and lead molybdate (at 56, 64, and 76 cm^{-1} for $PbWO_4$; and at 62 and 74 cm^{-1} for $PbMoO_4$); these lines are comparable in intensity with the internal vibration line $\nu_2(E)$ at ~330 cm^{-1}.

Data systematization brings us to the following conclusion: In the Raman spectra of some oxide materials belonging to the orthorhombic or tetragonal crystal system that contain nearly free anions and lead cations, lines appear at frequencies below 100 cm^{-1}, comparable in intensity with the lines of internal anionic vibrations.

Having inspected the literature relating to structural studies of various classes of lead-containing oxide materials, we found that similar strong lines were observed not only in our studied crystals. These lines, observed below 100 cm^{-1} in lead-containing oxide materials, were assigned to Pb–O stretching vibrations [8–10]. Most likely, such the high intensities of the Pb–O stretching vibration lines arise from the high covalence of Pb^{2+} bonding to oxygen [7]. We described a similar intensity redistribution effect in the spectra of isostructural crystals when reporting on our study of indium rare-earth orthoborates [11]. So, the abnormally strong Raman lines corresponding to external vibrations in some oxide crystals in the region of 100 cm^{-1}, can serve as evidence for the presence of high-covalence cations, specifically, Pb^{2+}, in these materials.

Noteworthy, Frost and Williams [12] identified lines in the range 100–4000 cm^{-1} in the spectra of lead-containing minerals, in particular, in phosgenite, so the lines in which we are interested were not in the focus of their publication. Rulmont [13] identified the lines that lie at 152 and 182 cm^{-1} in the phosgenite spectrum as Cl–Pb–Cl bending vibrations.

CONCLUSIONS

The Raman spectra of some lead-containing oxide compounds feature lines in the range below 100 cm^{-1} whose intensities are abnormally high for external vibrations and which are assignable to Pb–O stretching vibrations. The appearance of these lines in Raman spectra implies, with a high degree of certainty, the presence of lead in the compound.

We find it interesting to carry out similar investigations for other structural classes of crystals that con-

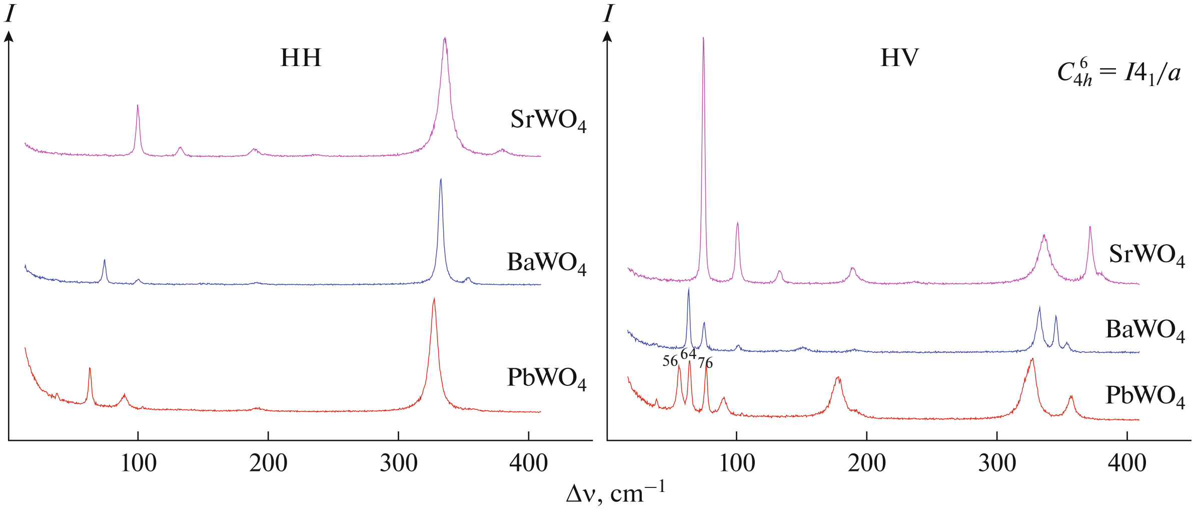

Fig. 3. Polarized Raman spectra of scheelite tungstate single crystals in the range 0–400 cm^{-1}. The figures denote the characteristic frequencies of Pb–O stretching vibrations.

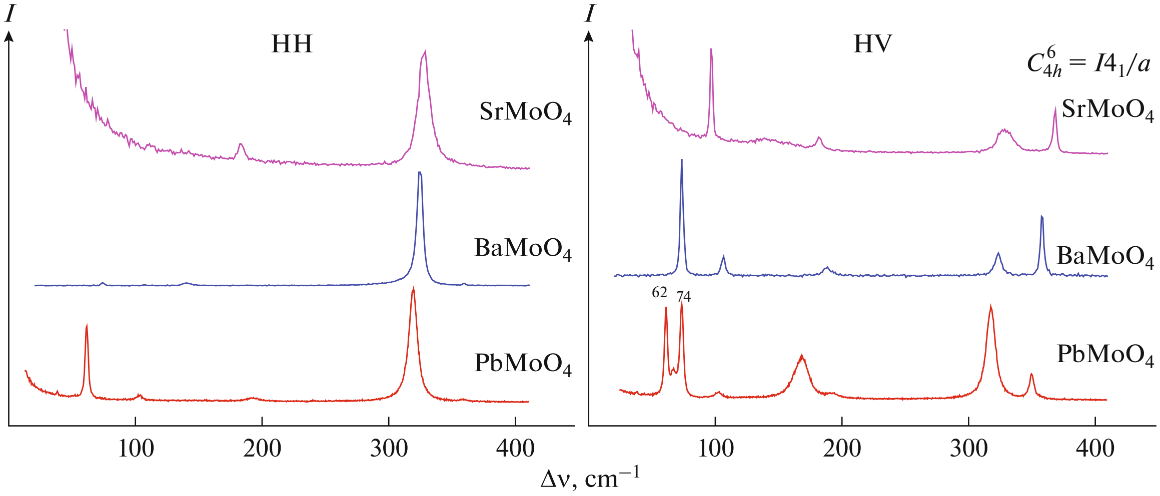

Fig. 4. Polarized Raman spectra of scheelite molybdate single crystals in the range 0–400 cm^{-1}. The figures denote the characteristic frequencies of Pb–O stretching vibrations.

tain triangular planar anions but belong to crystal systems of higher symmetries than the orthorhombic system. These materials are exemplified by the series of calcium, strontium, barium, and lead nitrates.

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