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Vibrational Structure in the Fluorescence Spectrum of Eu^{3+} in $KTaO_3$

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Vibrational satellite structure has been observed in the fluorescence spectrum of Eu^{3+} in the cubic perovskite $KTaO_3$. A comparison is made between the frequencies of vibrational peaks associated with the $^5D_0 \rightarrow {}^7F_1$ zero-phonon line at 77°K and observed or predicted lattice vibrational frequencies of $KTaO_3$. The $^5D_0 \rightarrow {}^7F_1$, $^7F_2$ regions of the fluorescence spectra of Eu^{3+} in $KTaO_3$ and $SrTiO_3$ at 77°K are also compared and discussed. The frequencies and structure of the satellite fluorescence spectra of Eu^{3+} in the two lattices are different.

INTRODUCTION

VIBRATIONAL satellite structure accompanying optical transitions of paramagnetic ions in crystals can yield information about the vibrational frequencies of the host lattice. For ferroelectric materials having the perovskite lattice structure, these vibrations, and in particular those of the lowest-frequency optical mode, have been shown to have important consequences for explanations of the dielectric properties. Recently the vibronic spectrum of Eu^{3+} in $SrTiO_3$, a crystal whose lattice dynamics have been relatively well investigated both experimentally and theoretically, was examined.[1] The frequencies of phonon-assisted fluorescence transitions were found to be in general agreement with lattice vibrational frequencies known from infrared and neutron-scattering spectroscopy. Here we present the vibronic spectrum associated with Eu^{3+} impurities in $KTaO_3$ observed in fluorescence.

Features of the vibronic spectrum in $KTaO_3$:Eu^{3+} which are of interest include (1) the frequencies and (2) relative intensities of the vibrational structure with respect to the zero-phonon transitions, the first being a measure of the vibrational frequencies of the host lattice, local vibrational modes, or combinations thereof, and the second the strength of the ion-lattice coupling. Potassium tantalate, unlike several other crystals having a perovskite lattice, remains paraelectric and exhibits no structural phase transition down to at least 4.2°K.[2,3] The vibrational structure in the fluorescence spectrum of Eu^{3+} in $KTaO_3$ is compared with the similar spectrum for $SrTiO_3$. Since K and Ta differ in both valence and mass from their counterparts in $SrTiO_3$, the lattice vibrational spectra of the two crystals are also expected to be different. It should be noted, however, that the vibrational frequencies which appear in vibronic spectra are those active at the site of the paramagnetic impurity. In the case of Eu^{3+} in $KTaO_3$, this impurity is both a charge and mass defect. Such defects may modify lattice frequencies and introduce local vibrational modes.

EXPERIMENTAL

Single crystals of Eu doped $KTaO_3$ were grown by a melt method using an excess of K_2CO_3 similar to the technique used by Miller[4] for the growth of $KNbO_3$. Although a seed was not used for growing the present sample, other work in this laboratory has produced longer and more well-developed $KTaO_3$ crystals following the procedure of Miller[4] and Wemple.[5] Based upon the phase diagram[6] for K_2CO_3-Ta_2O_5, a composition of 55 mole-percent K_2CO_3 and 45 mole-percent Ta_2O_5 was chosen. Eu was added in the form of 0.03 weight-percent Eu_2O_3. The materials were packed into a loosely covered platinum crucible and heated to 1400°C for four hours to ensure complete solution. The cooling rate from 1400 to 1100°C was 3°C/hr; the crucible was removed from the furnace at 1100°C. Portions of the melt were completely unusable, however several crystals ranging up to ~1 cm in the longest dimension were obtained. They exhibited a pale purple coloration. Attempts to add greater amounts of Eu_2O_3 were unsuccessful, the crystallization properties of $KTaO_3$ apparently preventing the incorporation of rare-earth ions to any greater extent.

The fluorescence of Eu^{3+} in a single crystal of $KTaO_3$ approximately 7 mm×7 mm×2 mm was examined using a 3.4 m Jarrell-Ash grating spectrometer and a cooled ITT FW-118 photomultiplier (S-1 photocathode). The spectrum was in general similar to that observed[1,7] for Eu^{3+} in $SrTiO_3$ above 110°K and consisted principally of transitions from the $^5D_0$ and $^5D_1$ excited states to levels of the ^7F ground term. A portion of the fluorescence spectrum in the vicinity of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions was recorded at 77°K in second order with a reciprocal dispersion of 4.8 Å/mm and is reproduced in Fig. 1. The spectrum as shown is

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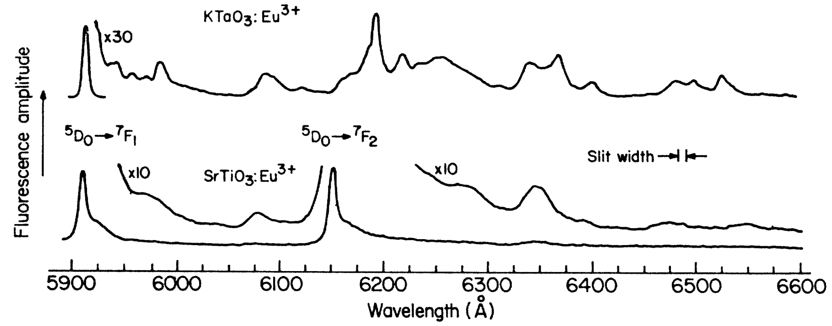

FIG. 1. A portion of the fluorescence spectrum of Eu^{3+} in $KTaO_3$ and $SrTiO_3$ at 77°K showing the vibrational structure associated with the $^5D_0 \to {}^7F_1$ and $^5D_0 \to {}^7F_2$ transitions.

uncorrected for the variation of spectral sensitivity which, however, was small and smooth. Additional spectra were recorded in sixth order. A tabulation of the principal fluorescence peaks observed from 5910 Å to 6550 Å are given in Tables I and II. The estimated accuracy is in the order of 3-5 cm^{-1}.

The fluorescence spectrum of Eu^{3+} in a crystal of $SrTiO_3$ used in previous studies[1,7] was also recorded under the above conditions and is included in Fig. 1 for comparison.

DISCUSSION

There are five atoms per unit cell of the cubic perovskite structure and hence 15 branches in the lattice vibrational spectrum. Phonons from several branches having various **k** vectors may contribute to the vibronic spectrum. The selection rules for vibronic transitions involving phonons at points of high symmetry in the first Brillouin zone of the perovskite lattice were derived previously[1] for impurity ions occupying lattice sites of cubic O_h point-group symmetry. For $KTaO_3$:Eu^{3+}, however, neither the location of the Eu^{3+} ions nor the nature of the charge compensation in $KTaO_3$ is established. Iron transition-metal elements are known from electron paramagnetic resonance[5,8] and optical spectra[5] to enter $KTaO_3$, presumably substitutionally at Ta sites. These ions are observed in trivalent, tetravalent, and pentavalent states and in sites having both cubic and axial crystal-field symmetry, the latter probably caused by a nearby, charge-compensating oxygen vacancy. Because of the large ionic radii of trivalent rare earths, ~1.0 Å, their substitution at K^+ sites (1.33 Å) rather than Ta^{5+} sites (0.73 Å) would be favored from size considerations. The question of the charge compensation and resulting symmetry of the local crystalline field remains in either case and with it the selection rules for vibronic transitions.

The fluorescence spectrum of $KTaO_3$:Eu^{3+} in Fig. 1 shows a $^5D_0 \to {}^7F_1$ zero-phonon line at 5910 Å, which is an allowed magnetic-dipole transition in intermediate coupling, and a very weak satellite structure. The vibrational sidebands for $SrTiO_3$:Eu^{3+}, in comparison, are more intense relative to the zero-phonon line, particularly near the zero-phonon line in the region corresponding to the acoustic and lower energy optical phonon branches. Only a single $^5D_0 \to {}^7F_1$ zero-phonon line was observed for $KTaO_3$:Eu^{3+} at 77°K. This is expected in a cubic crystalline field, although in an axial or lower symmetry field, the $(2J+1)$-fold degeneracy of $^7F_1$ would be reduced. (There was evidence of some noncubic crystal-field splitting of the $^5D_1$ fluorescent level.) The frequencies of vibrational satellites with respect to the $^5D_0 \to {}^7F_1$ zero-phonon line of $KTaO_3$:Eu^{3+} are given in Table I.

TABLE I. Wavelengths of peaks in the fluorescence spectrum of Eu^{3+} in $KTaO_3$ at 77°K and displacements from the $^5D_0 \to {}^7F_1$ zero-phonon line.

Wavelength (Å)	Displacement from zero-phonon line (cm^{-1})	Infrared frequencies (cm^{-1})
5910	0	
5925	42	43 (77°K)[c] 85.1(295°K)[a] (TO)
5936	74	
5941	88	
5954	125	
5966	158	
5977	189	192(LO)[b] 199(TO)[a]
6087	492	435(LO)[b]
6094	510	
6120	580	549(TO)[a] 910(LO)[b]

[a] Observed—Ref. 10.
[b] Predicted—Ref. 2.
[c] Predicted—see text.

TABLE II. Locations of peaks in the fluorescence spectrum of Eu^{3+} in $KTaO_3$ at 77°K.

Wavelength (Å)	Energy (cm^{1-})	Wavelength (Å)	Energy (cm^{-1})
6157	16 242	6341	15 770
6171	16 205	6369	15 701
6185	16 168	6401	15 623
6193	16 147	6456	15 489
6217	16 085	6483	15 425
6236	16 036	6499	15 387
6256	15 986	6526	15 323
6312	15 843		

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No large ${}^5D_0 \rightarrow {}^7F_2$ zero-phonon lines were found in $KTaO_3$. The zero-phonon ${}^5D_0 \rightarrow {}^7F_2$ line in $SrTiO_3$ at 6152 Å in Fig. 1 disappears for temperatures above 110°K, where the lattice becomes cubic and such transitions are forbidden, and only the vibronic structure remains.[1] These results, by themselves, suggest that Eu^{3+} ions may reside in $KTaO_3$ sites possessing inversion symmetry.

The wavelengths of peaks in the spectral region where ${}^5D_0 \rightarrow {}^7F_2$ vibrational structure is expected are given in Table II. Since the ${}^7F_2$ state is split even in a cubic field, a multiplicity of vibrational peaks in the ${}^5D_0 \rightarrow {}^7F_2$ fluorescence spectrum are possible. Some of the intensity in the vicinity of 6250 Å was found to arise from ${}^5D_1 \rightarrow {}^7F_4$ transitions. This was established by monitoring the fluorescence decay in the time domain as the spectrum was scanned. Since the fluorescence lifetimes of ${}^5D_0$ and ${}^5D_1$ differ by an order of magnitude,[9] the presence of fluorescence from either of these states is readily distinguishable. Peaks in the vicinity of 6500 Å may include weak ${}^5D_0 \rightarrow {}^7F_3$ transitions. The combination of the above factors complicates any interpretation of the ${}^5D_0 \rightarrow {}^7F_2$ vibrational structure.

The frequencies of vibrational peaks with respect to the ${}^5D_0 \rightarrow {}^7F_1$ zero-phonon line can be compared with the frequencies of $\mathbf{k} \approx 0$ phonons in pure $KTaO_3$ determined by infrared spectroscopy. There are three triply degenerate infrared-active normal modes of vibration for the perovskite lattice. The three transverse optical (TO) mode frequencies measured by Miller and Spitzer[10] are included in Table I together with the estimated[2] frequencies of the related longitudinal optical (LO) modes. Peaks are observed in the vibronic spectrum which in some cases correspond reasonably well with these $KTaO_3$ lattice frequencies, but additional peaks are also present which may originate from phonons of different frequencies from other points in the Brillouin zone, or modified local mode frequencies. The highest-frequency LO branch at $\mathbf{k} \approx 0$ is predicted to occur at ≈ 6250 Å. Although peaks are observed in this region, they may be associated with ${}^5D_0 \rightarrow {}^7F_2$ or ${}^5D_1 \rightarrow {}^7F_4$ transitions. In general, because of our incomplete knowledge of the lattice vibrational frequencies and the site of Eu^{3+} in $KTaO_3$, any explicit correlations between vibronic peaks and lattice or local mode frequencies would be correspondingly uncertain at this time.

One vibrational mode of particular interest is the lowest frequency TO branch at $\mathbf{k}=0$. For crystals in which the static dielectric constant exhibits a Curie-Weiss law behavior, the frequency of this mode is predicted[11,12] to vary with temperature as $(T\text{-}T_c)^{1/2}$, where T_c is the Curie temperature. This has been observed for $SrTiO_3$.[13,1] The dielectric-constant data for $KTaO_3$ can be fitted to a Curie-Weiss law above 30°K (the Curie temperature for pure $KTaO_3$ appears to be less than 1.6°K[2]). The predicted frequency of the temperature-dependent TO mode, which is assigned to the 85.1 cm^{-1} vibration at room temperature, is 43 cm^{-1} at 77°K. A small peak is observed at 42 cm^{-1}; however, it is on the shoulder of the very much larger zero-phonon line. (In contrast, in $SrTiO_3$:Eu^{3+} this mode generates the most intense vibronic transition and is clearly resolvable,[1] although not under the conditions used in Fig. 1.) Since the zero-phonon line broadens with increasing temperature, it was not possible to follow this small peak with the signal level available. A search was also made for peaks in the region of the ${}^5D_0 \rightarrow {}^7F_2$ vibrational structure which shift with temperature. Spectra recorded at 77, 200, and 300°K were examined but no temperature-dependent bands were detected.

ACKNOWLEDGMENT

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[9] The temperature dependence of the fluorescence lifetime of the ${}^5D_0$ level of Eu^{3+} in $KTaO_3$ is similar to that observed in $SrTiO_3$. (Ref. 7). It is 1.3 msec at liquid-nitrogen temperatures and decreases to ≈ 1.0 msec at 300°K with a more rapid decrease with increasing temperature thereafter.

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