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Photoluminescence of Cr-Doped $CaTiO_3$

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At 4 and 77 K, photoluminescence from nominally undoped and 0.0025% Cr-doped $CaTiO_3$ shows identical spectra in the infrared with an intensity ratio of 1:2. The emission is attributed to the $^2E \rightarrow {}^4A_2$ transition of the Cr^{3+} ion at a Ti^{4+} site. At 4 K it consists of a single no-phonon line at 1.744 eV of half-width 1.5 meV and a complex vibronic spectrum which is anomalously intense. Data at 77 K show a 2-meV splitting of the ^2E state. The absorption spectrum of $CaTiO_3$:Cr is dominated by a "background absorption" by unknown defects. From the coincidence of the excitation spectrum with the absorption spectrum, we conclude that the excitation is dominated by absorption by these unknown defects which transfer energy into Cr^{3+}. In undoped $CaTiO_3$ a single-exponential decay of the emission is reported, with decay time 700 μsec. In $CaTiO_3$:0.0025% Cr, on the other hand, two exponentials with decay times 700 μsec and 11 msec were observed. The former is assigned to Cr^{3+}, the latter to the time of energy transfer from defects responsible for the background absorption to the Cr^{3+}. We also report a visible emission consisting of a broad structureless band centered at 2.7 eV, with half-width 0.7 eV. Presumably, it is recombination radiation caused by the recombination of a free charge carrier with a trapped charge at an unknown defect. Its excitation spectrum gives a band gap for $CaTiO_3$ of 3.70 eV at 4 K.

I. INTRODUCTION

In this paper, we report the spectra of emission, excitation of emission, and the optical absorption spectrum of $CaTiO_3$:Cr. The results may be of some interest in complementing recently accumulated data on the spectroscopy of transition-metal ions in the titanates, namely, $SrTiO_3:Cr^{3+}$,[1–3] $TiO_2:Cr^{3+}$,[4] Mg_2TiO_4: Cr^{3+},[5] $Mg_2TiO_4:Mn^{4+}$,[6] $ZnTiO_4:Mn^{4+}$,[6] $MgTiO_3:Mn^{4+}$,[7] and $SrTiO_3:Mn^{4+}$.[1]

$CaTiO_3$ is the mineral perovskite. It is orthorhombic with space group *Pcmn* (D_{2h}^{16}).[8] By analogy with other systems, $SrTiO_3:Cr^{3+}$ and $TiO_2:Cr^{3+}$, for example, in which the valency of the Cr ion has been established as Cr^{3+} by electron-spin-resonance measurements, we shall *assume* that in $CaTiO_3$ chromium also enters as Cr^{3+}. On the basis of ionic radii it is expected that the Cr^{3+} substitutes for a Ti^{4+} ion in $CaTiO_3$.

Probably because of the difficulty of synthesizing high-quality single crystals of $CaTiO_3$,[9] few of its physical properties have been measured. From the scant data available, these appear to be similar to $SrTiO_3$. Thus, Rupprecht and Bell[10] measured the static dielectric constant as a function of temperature and conclude that $CaTiO_3$ is a paraelectric obeying a Curie-Weiss law with a negative Curie temperature. $SrTiO_3$ exhibits similar behavior, except that its Curie temperature is positive.[10] Linz and Herrington[11] measured the refractive index in the visible region, the static dielectric constant as a function of temperature, and the optical absorption. Perry *et al.*[12] measured the infrared reflection and transmission spectra and list the infrared active modes. Finally, there is a brief reference to $CaTiO_3$: Eu^{3+} in a survey by Yamamoto *et al.*[13] of the vibronic structure in luminescence spectra of rare-earth ions in $SrTiO_3$, $BaTiO_3$, and other perovskites.

The experimental technique used in this study has been described previously.[2]

II. RESULTS AND DISCUSSION

The specimens used in this work were obtained through the courtesy of the National Lead Company. They exhibited intense lamellar twinning of random orientation. Consequently, polarized spectra using the anisotropy of $CaTiO_3$ could not be obtained. Three specimens, one nominally undoped, the other two doped with 0.0025% Cr_2O_3 and 0.03% Cr_2O_3, respectively, were used. The infrared emission spectrum of the undoped and $CaTiO_3$:0.0025% Cr samples are shown in Fig. 1. They are identical, except that the Cr-doped specimen shows a factor of 2 increase of the emission intensity. It should be remarked that experience with $SrTiO_3$ and TiO_2 has shown that nominally undoped specimens contain spectrochemically undetectable traces of Cr which, nevertheless, are easily detected as fluorescence from the Cr^{3+} ion. We assume that this is duplicated in $CaTiO_3$, although, in contrast, comparable levels of Cr doping in $SrTiO_3$ and TiO_2 increased the emission by a factor of ~100 over that of undoped specimens.[1,2,4] We believe that the reason for the smaller increase of the emission of $CaTiO_3$:0.0025% Cr over that of $CaTiO_3$ is that the absorption spectrum of $CaTiO_3$:0.0025% Cr, shown in Fig. 2, overlaps the emission spectrum. In support of this, we find that the $CaTiO_3$:0.03% Cr showed no infrared emission. Its absorption spectrum is also shown in Fig. 2 and is seen to completely overlap the emission spectrum.

With some reservation, we propose that the emission spectrum shown in Fig. 1 is due to a $^2E \rightarrow {}^4A_2$ transition of the Cr^{3+} with phonon cooperation. The no-phonon lines, A_1 and A_2 in this view, are the commonly seen R line doublet, in this case due to the crystal field splitting of the parent ^2E state into two states by a field of D_{2h} symmetry. At 4 K, of course, only the lowest of the two ^2E states is populated, giving a single no-phonon line as shown in Fig. 1. We suggest this interpretation

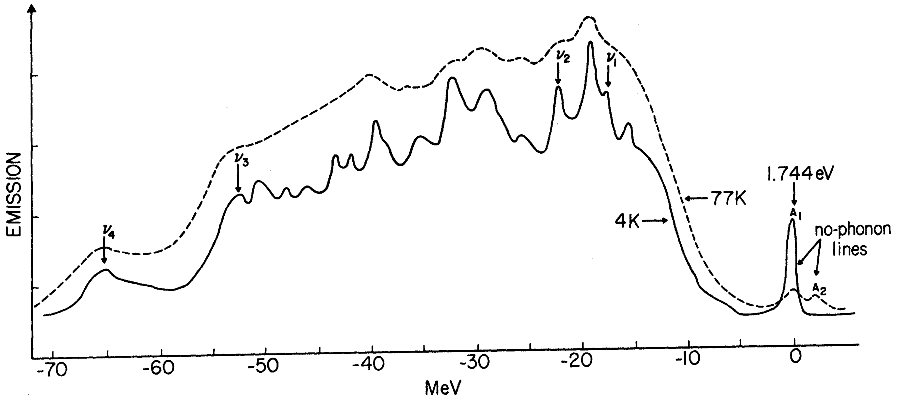

FIG. 1. Infrared emission spectrum at 4 and 77 K plotted with respect to no-phonon line at 1.744 eV at 4 K.

with reservations because the rather intense vibronic participation is not typical of similar systems in which the Cr^{3+} emission has been identified as a ${}^2E \rightarrow {}^4A_2$ transition. It is conceivable that the emission is not that of Cr^{3+}, a possibility we do not rule out, but think unlikely. Alternatively it is possible that the lowest excited state of the Cr^{3+} ion is not the ${}^2E$ state but another state of the Cr^{3+} ion. This question is treated with some caution because of the authors' experience with $TiO_2:Cr^{3+}$ [4] in which the lowest excited state of the Cr^{3+} proved to be the ${}^4T_2$ state. The ${}^4T_2 \rightarrow {}^4A_2$ transition in $TiO_2:Cr^{3+}$ displays sharp no-phonon lines and vibronics, the intensity of which is 10^4 that of the no-phonon lines. In this respect, $CaTiO_3:Cr^{3+}$ appears to be intermediate to $SrTiO_3:Cr^{3+}$ and $TiO_2:Cr^{3+}$.

Vibronic transitions can involve lattice phonons and defect phonons. The vibronic structure shown in Fig. 1 is of considerable complexity and an analysis is frustrated by lack of information on the phonon dispersion curves. In $SrTiO_3:Cr^{3+}$,[2] for example, the phonon dispersion curves showed that the principal contribution to the vibronics is that of lattice phonons. In contrast, the vibronics of Cr^{3+} in TiO_2 [4] are mainly defect phonons. In $CaTiO_3:Cr^{3+}$, on the other hand, the data are inconclusive as to whether the vibronics are lattice phonons, defect phonons, or a combination of the two. We content ourselves by observing that the infrared active phonons listed by Perry *et al.*[12] at 18, 22, 55, and 68 meV may be the phonons giving rise to the vibronics labeled ν_1, ν_2, ν_3, and ν_4, respectively, in Fig. 1. It should be remarked that our assignment of ν_1 to the infrared active phonon observed by Perry *et al.* at 18 meV and 300 K is doubtful. These authors assign this phonon to the temperature-dependent "soft mode" which is expected to move to lower energies at 4 K, at which temperature our observations were made.

It is unlikely that the strong broad-band absorption shown in Fig. 2 is due to the Cr^{3+} ion alone—the absorption coefficients are too large for the Cr concentration. Here we meet a situation similar to that observed in $SrTiO_3:Cr^{3+}$ [1] and $TiO_2:Cr^{3+}$.[4] In these materials it was suggested that the absorption coefficient is additively composed of two components: absorption due to Cr^{3+} and a background absorption due to unknown defects induced by the Cr during the growth process. In $SrTiO_3:Cr^{3+}$ and $TiO_2:Cr^{3+}$ the background absorption is dominant and we assume this is also the case in $CaTiO_3:Cr^{3+}$. Be that as it may, we summarize by noting that the absorption spectrum of $CaTiO_3:Cr^{3+}$ shows characteristics similar to those of $SrTiO_2:Cr^{3+}$ and $TiO_2:Cr^{3+}$, and that the underlying reason for this, presently unknown, is very likely the same in all these examples.

The background absorption is of more than cursory interest because it contributes to excitation of the Cr^{3+}, as shown by the excitation spectrum of the total infrared emission shown in Fig. 2. This property is again shared by $SrTiO_3:Cr^{3+}$ and $TiO_2:Cr^{3+}$, and we conclude as we did in these materials that there is energy transfer from the defects inducing the background absorption to the Cr^{3+}. The mechanism of energy transfer[14]—whether a "cascade" mechanism, resonant energy transfer, or a

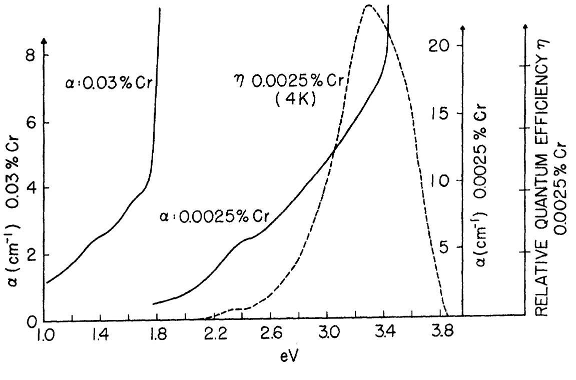

FIG. 2. Absorption spectrum of $CaTiO_3$:0.0025% Cr and $CaTiO_3$:0.03% Cr taken at 300 K. Dashed curve is relative quantum efficiency of excitation of the total emission shown in Fig. 1 at 4 K.

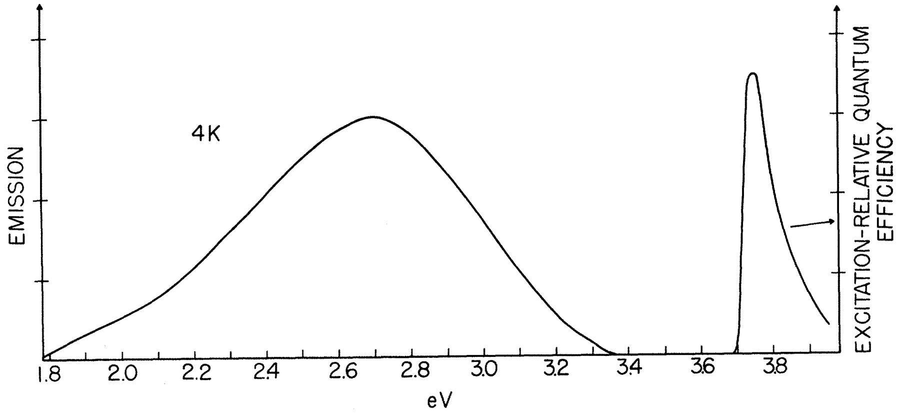

FIG. 3. Visible emission and excitation of visible emission at 4 K.

transfer of energy via the bands by free electrons and holes—is presently not clear and requires further study.

Further evidence for energy transfer is contained in the lifetime measurements. We find the decay of the infrared emission of undoped CaTiO$_3$ at 4 and 77 K is a single exponential with a decay time of 700 μsec. In contrast, the decay of CaTiO$_3$:0.0025% Cr^{3+} exhibits two exponentials, one with a decay time of 700 μsec, the other 11 msec. We conclude the former is the lifetime of the ^2E state of Cr^{3+}, the latter is the rate at which energy is transferred from the defects to the Cr^{3+}.

In addition to the infrared emission discussed so far, a broad structureless band peaking at 2.7 eV, of half-width 0.7 eV, was observed in undoped CaTiO$_3$ and CaTiO$_3$:0.0025% Cr. It is shown together with its excitation in Fig. 3. We suggest that the emission is recombination radiation resulting from the recombination of a free-charge carrier with a charge trapped at an unknown defect. The threshold of excitation at 3.7 eV is probably the onset of the production of free-charge carrier via band-to-band transitions and is thus the band gap of CaTiO$_3$ at 4 K. Attempts to confirm this by the simultaneous measurement of the photocurrent were unsuccessful. This visible emission has an analog in SrTiO$_3$ [2] but not in TiO$_2$.

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[1] S. E. Stokowski and A. L. Schawlow, Phys. Rev. Letters **21**, 965 (1968); Phys. Rev. **178**, 457 (1969).

[2] Ludwig Grabner, Phys. Rev. **177**, 1315 (1969).

[3] W. J. Burke and R. J. Pressley, Phys. Rev. **182**, 395 (1969); Solid State Commun. **7**, 1187 (1969).

[4] Ludwig Grabner, S. E. Stokowski, and W. S. Brower, Jr., Phys. Rev. (to be published).

[5] R. Dittmann, D. Hahn, and J. Stade, Z. Naturforsch. **24a**, 1323 (1969).

[6] R. Dittmann and D. Hahn, Z. Physik **207**, 484 (1967).

[7] G. Villela, Y. Sackali, A. Lauat, J. Paris, and F. Gaume-Mahn J. Phys. Chem. Solids **30**, 2599 (1969).

[8] H. F. Kay and P. C. Bailey, Acta Cryst. **10**, 219 (1957).

[9] Leon Merker, J. Am. Ceram. Soc. **45**, 366 (1962).

[10] G. Rupprecht and R. O. Bell, Phys. Rev. **135**, A748 (1964).

[11] A. Linz, Jr., and K. Herrington, J. Chem. Phys. **28**, 824 (1958).

[12] C. H. Perry, B. N. Khanna, and G. Rupprecht, Phys. Rev. **135**, A408 (1964).

[13] Hajime Yamamoto, Shoji Makishima, and Shigeo Shionoya, J. Phys. Soc. Japan **23**, 1321 (1967).

[14] Clifford C. Klick and James H. Schulman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5.