experimentally determined functions of the type $\lambda(\tau)$, each of which can be determined to an accuracy of ± 0.02.

All of the experimentally observed correlation functions $\lambda(\tau_1,\tau_2)$ were observed to be approximately of the form $\lambda(\tau_1,\tau_2)=\lambda(0,0)\exp(-|\tau_1|/T_c')\exp(-|\tau_2|/T_c')$ as shown by the example in Fig. 9. Well below threshold T_c' was observed to be equal to T_c, the second-order intensity fluctuation correlation decay constant. As the threshold of oscillation was approached, T_c' was observed to depart increasingly from T_c. [Table I lists the decay constants T_c and T_c' of the correlation function $\lambda(\tau)$ and $\lambda(\tau_1,\tau_2)$ with respect to τ, τ_1, and τ_2.]

Figure 10 is a plot of T_c' as a function of mean laser intensity. The solid curve represents the behavior of T_c in the threshold region. The values of T_c that resulted from measurements made to determine the function $\lambda(\tau)$ to be used in calculating $\lambda(\tau_1,\tau_2)$ from Eq. (6) were in agreement with the solid curve. No theoretical decay constants T_c' for the third-order intensity fluctuation correlation functions as a function of mean laser intensity in the threshold region have been calculated so far.

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Dielectric Relaxation in Alkaline-Earth Fluoride Crystals*

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Dielectric absorption has been investigated over a temperature range from −34 to 450°C and a frequency range from 1 to 10^6 cps for doped CaF_2, BaF_2, and SrF_2 crystals. The activation and association energies for the dipolar complexes have been determined. The activation energy for CaF_2 doped with 0.01-mole% YF_3 was found to be 1.17 eV.

I. INTRODUCTION

THE effects produced by the doping of ionic crystals with known concentrations of aliovalent cations can be investigated using various techniques. Several investigations have shown that the predominant intrinsic defects in CaF_2-type crystals are Frenkel anion pairs.[1–3] When a trivalent ion replaces a positive divalent ion in the lattice of an alkaline-earth fluoride crystal, a singly charged negative ion interstitial may be introduced into a next-nearest-neighbor position as a charge compensator. A dipolar complex results from the cation impurity possessing an extra positive charge, and the interstitial possessing an effective negative charge.

Both Zintl and Udgard[1] and Short and Roy[2] have shown that a dissolved trivalent yttrium ion is accompanied by an interstitial fluorine ion. With the aid of conductivity experiments, Ure[3] has shown that a trivalent yttrium ion is associated with an interstitial fluorine ion, and a sodium ion is associated with a fluorine vacancy. Also, electron paramagnetic studies of rare-earth-doped alkaline-earth fluoride crystals have demonstrated that the rare-earth site has tetragonal symmetry which may be explained by the presence of a charge compensating fluorine interstitial at a nearest-neighbor position.[4]

Dielectric measurements on the alkaline-earth fluorides have been previously reported.[5–7] Our investigations have been principally concerned with dielectric relaxation in doped CaF_2, BaF_2, and SrF_2.[8] The phenomena observed can be described in terms of the relaxation mechanisms originated by Debye[9] and later applied to crystal imperfections by Breckenridge.[10] Using the method described by Lidiard[11] the expression for an alkaline-earth fluoride crystal of the loss tangent, for a single loss mechanism possessing a unique relaxation time is

$$\tan\delta=(4\pi a^2e^2N_ip/3kT\epsilon)\omega\tau/(1+\omega^2\tau^2)\,,$$

where a is the anion-cation separation, e is the electronic charge, N_i is the concentration of the impurity ion, p is the degree of association, k is Boltzmann's constant, T is the absolute temperature, ϵ is the static dielectric constant of the crystal, ω is the angular frequency of the applied electric field, and τ is the relaxation time. The

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‡ Based in part on work submitted by M.S.M. as a thesis in partial fulfillment of the requirements for the doctoral degree at Boston College.

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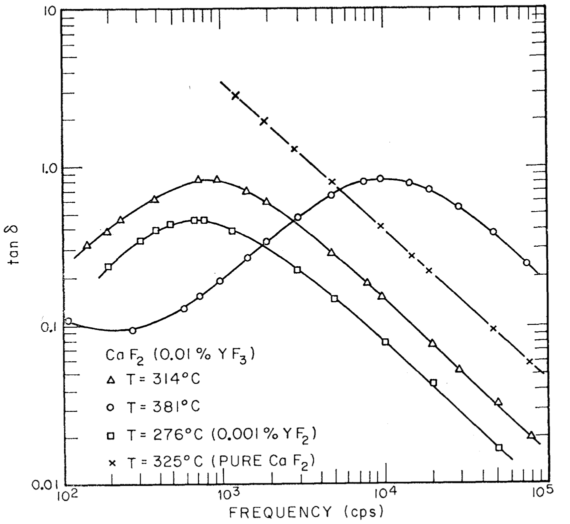

FIG. 1. Loss tangent versus the frequency for pure CaF_2 and for CaF_2 doped with 0.01- and 0.001-mole% YF_3.

activation energy for the dipolar rotation can be determined from the frequency and temperature dependence of the relaxation peaks.

Dielectric absorption has been investigated over a temperature range from −34 to 450°C, and a frequency range from 1 to 10^5 cps. Single Debye relaxation curves were obtained, except in the case for $CaF_2(YF_3,NaF)$ where two charge compensator effects were observed. From these measurements the activation and association energies for the complexes were obtained.

II. EXPERIMENTAL PROCEDURES

CaF_2, SrF_2, and BaF_2 single crystals doped with YF_3 and NaF were grown by Optovac Inc., and the pure crystals were obtained from the Harshaw Chemical Company. The sample crystals were in the shape of cylindrical disks with flat parallel faces. The diameters of the crystals ranged from 0.5 to 1.0 in., and the thickness varied from 0.08 to 0.3 in. Conducting films of gold or silver were evaporated on the flat surfaces of the sample crystal to ensure good electrical contact between the applied electrodes and the crystal.

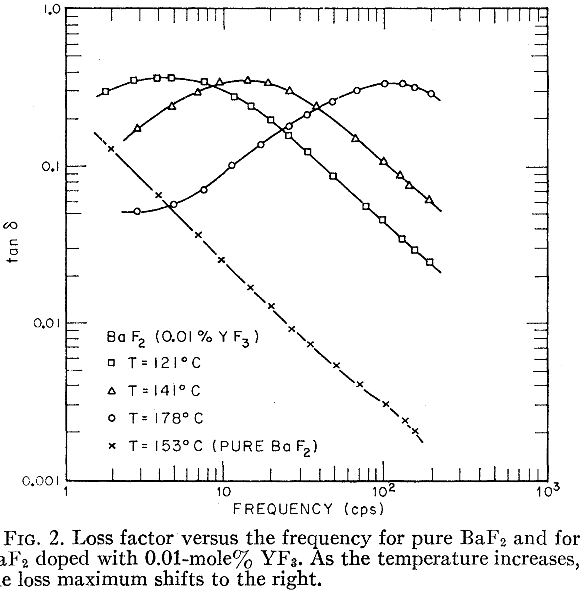

FIG. 2. Loss factor versus the frequency for pure BaF_2 and for BaF_2 doped with 0.01-mole% YF_3. As the temperature increases, the loss maximum shifts to the right.

Doped crystals of varying thickness were examined. The position and magnitude of the loss tangent peak was independent of the thickness. This implies that interfacial polarization effects were not the cause of the observed absorption peaks. Also, measurements performed on pure crystals showed no relaxation losses under identical conditions. These results indicate that the loss peaks are due to impurities.

The sample crystal was placed between two silver electrodes in a cell containing dry nitrogen. A chromel-alumel thermocouple located in the upper electrode was used to measure the temperature. Each run consisted of maintaining the sample at a fixed temperature with the loss measured as a function of frequency.

The frequency range from 10^2 to 10^5 cps was measured by the General Radio 1615A Bridge System, and the range from 1 to 200 cps was measured on a bridge based on the design of Scheiber.[12] By using a three terminal bridge, the loss and capacitance due to the electrodes with respect to ground were excluded from the measurements.

III. EXPERIMENTAL RESULTS

Figure 1 presents the dielectric loss tangent as a function of frequency for CaF_2. For the undoped crystal, the straight-line results from the loss due to the conductivity of the unassociated ions. The other three

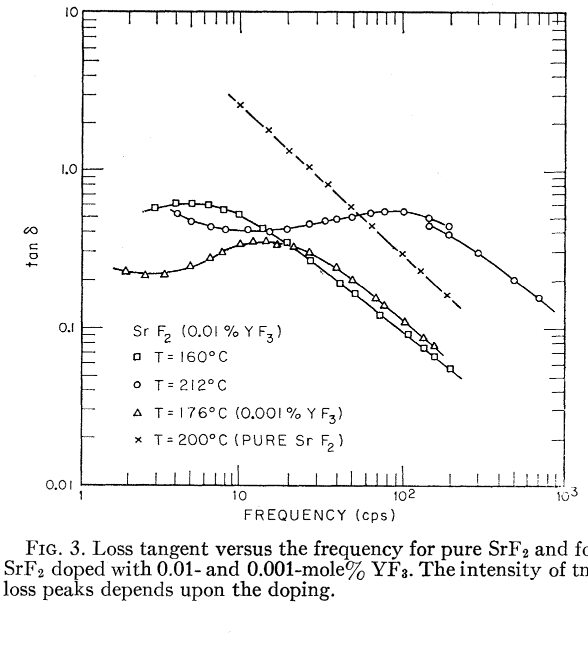

FIG. 3. Loss tangent versus the frequency for pure SrF_2 and for SrF_2 doped with 0.01- and 0.001-mole% YF_3. The intensity of tne loss peaks depends upon the doping.

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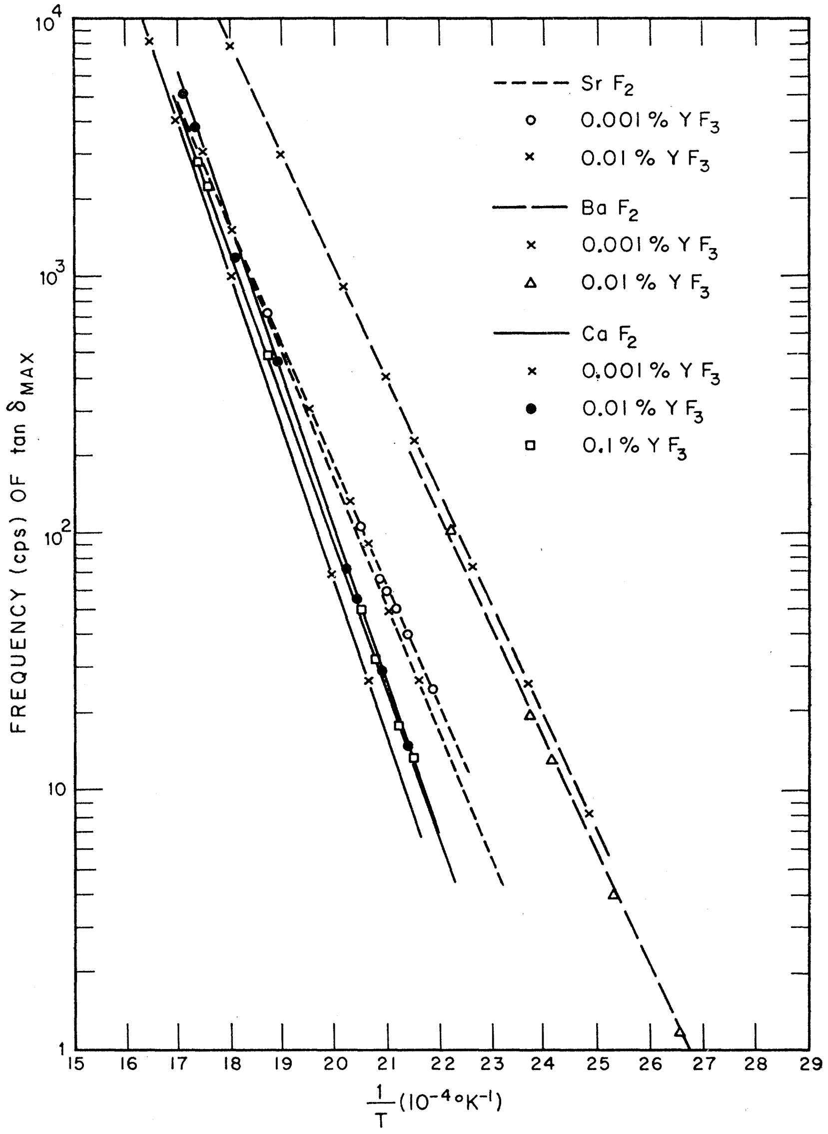

FIG. 4. Frequency at which the maximum of the loss tangent occurs versus the reciprocal of the absolute temperature. From the slope of the straight line, the ctivation energy is calculated.

curves result from CaF_2 containing 0.01- and 0.001-mole% YF_3. The loss tangent curves can be fitted with a Debye curve of the form $\tan\delta = A\omega\tau/(1+\omega^2\tau^2)$ whose maximum occurs when $\omega\tau = 1$. The loss tangent maximum shifts to higher frequencies as the temperature increases.

Figures 2 and 3 show the results for yttrium-doped BaF_2 and SrF_2. Here again the loss peak shifts as a function of temperature, and the undoped samples do not exhibit a loss peak in the same frequency and temperature range. In Fig. 3, the data for $T = 212$°C are a composite of measurements from the two different bridge systems.

The frequency f_m at which the maximum loss occurs, is shown in Fig. 4 as a function of temperature. A plot of $\ln f_m$ versus $1/T$ is linear, indicating a relationship of the form $f_m = 1/\tau = \nu e^{-E/kT}$, where E is the activation energy for the relaxation process, ν is a frequency factor, and k is Boltzmann's constant. The activation energy is given by the slope of the linear plots. For CaF_2 doped with 0.01-mole% YF_3 the above relation can be written as $1/\tau = (3.3 \times 10^{13}\ \text{cps}) e^{-(1.17\ \text{eV})/kT}$. Table I

TABLE I. Activation and association energies for crystals doped with either YF_3 or YF_3-NaF. As the lattice constant increases, the activation and association energies decrease.

Crystal	Activation energy (eV)	Association energy (eV)	Lattice constant (Å)
$CaF_2(YF_3)$	1.16±0.08	0.12 ±0.02	5.46
$SrF_2(YF_3)$	1.01±0.02	0.09 ±0.03	5.81
$BaF_2(YF_3)$	0.86±0.02	0.06 ±0.01	6.21
$CaF_2(YF_3,NaF)$	1.20±0.02	0.12 ±0.02	
	0.20±0.02	0.045±0.01	

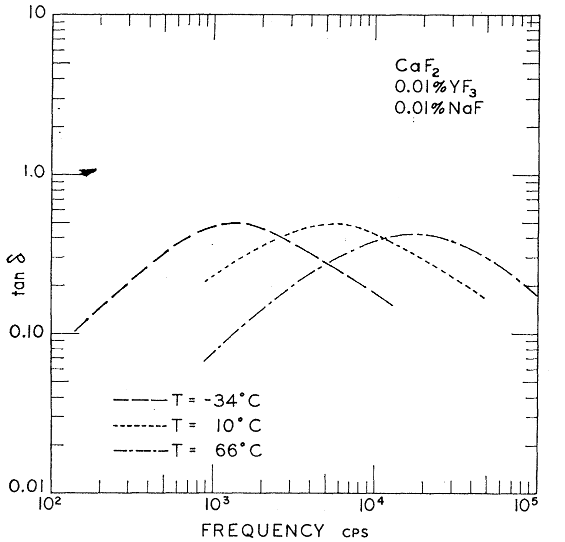

FIG. 5. Loss tangent versus the frequency for CaF_2 doped with 0.01- and 0.01-mole% NaF. The second set of relaxation peaks is shown.

presents the activation energies for yttrium-doped CaF_2, SrF_2, and BaF_2 crystals obtained from Fig. 4. The results in this table shows the trend that the activation energy decreases as the lattice constant increases.

In the sample of CaF_2 containing both yttrium and sodium, a second set of relaxation peaks have been observed (Fig. 5). For a given temperature the second loss peak has a shorter relaxation time, with an activation energy of 0.2 eV. The second peak is associated with the presence of the sodium impurity.

The measurements were all made at constant temperature with varying frequency. Thermodynamic equilibrium is assured by maintaining the sample at a fixed temperature for at least several hours until the magnitude of the loss tangent peak reached a constant value. From the height of the loss peak, one can deduce the degree of association at any temperature T. A plot of $\ln[p/(1-p)^2]$ versus $1/T$ yields a straight line whose slope is given by E_a/k, where p is the degree of association and E_a is the association energy.[11] These plots are shown in Figs. 6–8 and the association energies are listed in Table I. The errors involved in the association energy are due to the restricted temperature range used and to the lack of sensitivity of the peak height to concentration and temperature. Table I indicates that the association energy decreases as the lattice constant increases. This decrease in association energy can be expected even from a simple Coulomb potential model, where the binding energy decreases as $1/r$. Also, the association energy of the Y^{3+}-F^- complex is approximately twice that of the Y^{3+}-Na^+ complex. This implies that the length of the Y^{3+}-F^- complex is half that of the Y^{3+}-Na^+ complex. The model used to describe these results will be explained in a later section.

TABLE II. Effect of impurity concentration on the linewidths of the loss peaks.

Nominal mole% doping of YF_3 in CaF_2	0.001	0.01	0.1	1.0
% deviation from a Debye curve	1–4	8–10	20	40

The width at half-maximum increases as the doping concentration increases. Table II illustrates the increase in width at half-maximum in $CaF_2(YF_3)$ relative to a theoretical Debye curve. For a given yttrium concentration there is also a slight narrowing of the linewidth as the temperature increases. This effect may be attributed to at least two sources, one of which may be associated with the variation of perfection of the crystal in the vicinity of the dipoles. This will give rise to a distribution of relaxation times and lead to a broadening of the absorption peak. The second possibility is the effect of dipoles in excited states; that is, complexes of higher dipole moments. It should also be observed that the intensity of the peaks decreases as the doping concentration decreases. However, the intensity is not proportional to the nominal doping concentration.

IV. DISCUSSION

A simple way to view the fluorite lattice is as follows: The fluorine ions form a simple cubic lattice with divalent cations at the center of alternate cubes. Scouler and Smakula[13] have shown that trivalent yttrium impurity enters the fluorite lattice substitutionally in place of the divalent cation. This has also been shown by

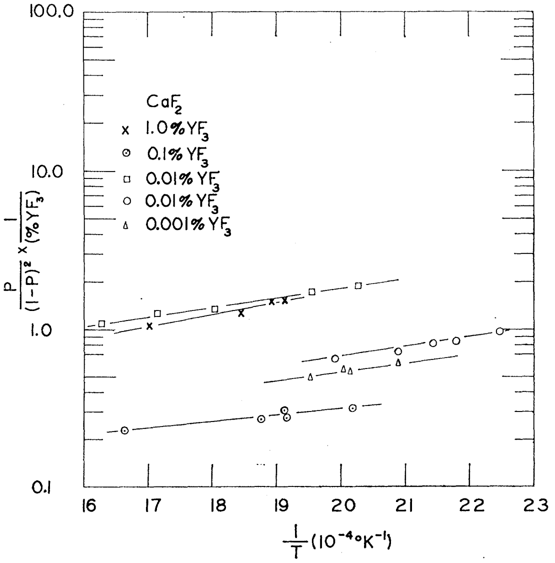

FIG. 6. Probability for association versus the reciprocal of the absolute temperature for CaF_2 doped with YF_3. From the slope of the straight line, the association energy is calculated.

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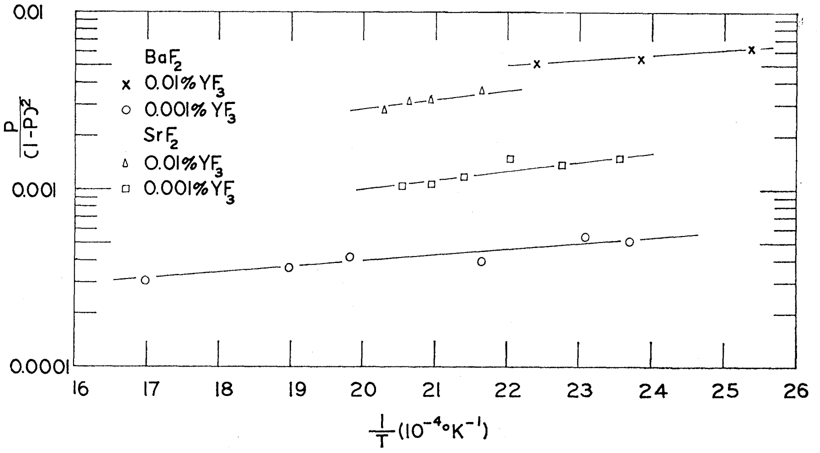

FIG. 7. Probability for association is plotted against the reciprocal of the absolute temperature for SrF_2 and BaF_2 doped with YF_3. The association energy is calculated from the slope of the straight line.

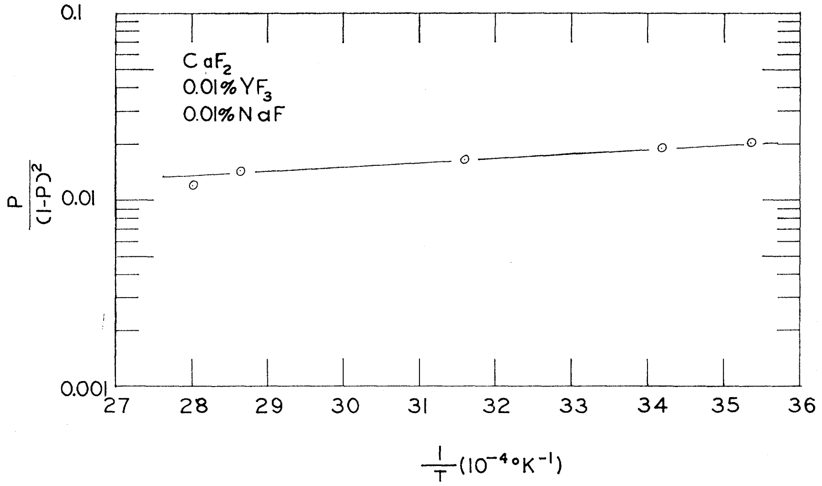

FIG. 8. Probability for association versus the reciprocal of the absolute temperature for CaF_2 doped with YF_3 and NaF. From the slope of the straight line, the association energy is calculated.

McDonough and Chen[14] from the Mössbauer effect of trivalent iron in CaF_2. The extra charge of the Y^{3+} ion is normally compensated by a F^- interstitial at the center of the normally vacant cube. It is this dipole system that gives rise to the dielectric relaxation peak with activation energy of 1.16 eV and an association energy of 0.12 eV. The activation energy represents the migration barrier of the F^- interstitial moving between the six possible octahedrally located positions about the trivalent ion. Although the value of the activation energy agrees with the value of Southgate,[7] our values for the activation energy and association energy are lower than the values found by Ure.[3] The results of additional dielectric relaxation measurements performed on doped alkaline-earth fluoride crystals have shown that as the ionic radius of the impurity ion decreases the activation energy decreases.[15]

The model for $CaF_2(YF_3\text{-}NaF)$ is as follows: The Y^{3+} ion enters the lattice substitutionally and is compensated by a Na^+ also located at a normal divalent cation site.[16] The complex of Y^{3+}-Na^+ should involve a smaller activation energy, since the smaller sodium ions should be more mobile than the larger fluorine ions. The activation energy for this system is 0.2 eV and the association energy is 0.045 eV, about half that of the Y^{3+}-F^- system. This is consistent with the proposed models since the separation for Y^{3+}-Na^+ is twice that for the Y^{3+}-F^- system.

V. CONCLUSION

Our results have shown that dielectric relaxation measurements may be made on CaF_2, BaF_2, or SrF_2 crystals doped with either YF_3 or YF_3-NaF. For the $CaF_2(YF_3\text{-}NaF)$ crystals, the two sets of relaxation peaks found were due to the Y^{3+}-F^- and Y^{3+}-Na^+ complexes. From the relaxation measurements, the activation and association energies for the dipolar complexes were obtained. The activation and association energies are characteristic of the aliovalent impurities and their charge compensators, and may be used as a means of identifying impurities in ionic crystals.

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