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Analogs of the Rose Center in the Alkaline Earth Fluorides: Production by Hydrolysis and Identification by Raman Spectroscopy

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A family of molecular centers of the type $(RO_2M)^{2+}$ is shown to exist in the alkaline earth fluorides MF_2 (M = Ca, Sr, Ba) doped with R = Sc, Y, Lu, Ho when these crystals have been hydrolyzed and subsequently X-rayed. The centers were identified with the aid of Raman spectroscopy and, in the past, with electron paramagnetic resonance (EPR).

Introduction

Since the work of Stockbarger (*1*) and Bontinck (*2*) was published it is known that CaF_2 crystals are easily hydrolyzed at high temperatures in an atmosphere which contains water. Stockbarger showed that adding PbF_2 to the melt during growth of CaF_2 gives transparent crystals. Bontinck investigated hydrolyzed crystal surfaces with infrared spectroscopy. Subsequently, several ESR and ENDOR studies have been published on *RE* ions in hydrolyzed alkaline earth fluoride crystals (*3–5*). Oxygen associated with the *RE* ions is detected by the magnetic *f* electron (*5*) of the *RE* through the effects of the crystal field. Recently Catlow (*6*) analyzed theoretically some of the available experimental results about hydrolyzation.

The fact that oxygen also plays a very important part in many color centers has been known only for a comparatively short time. The first of these centers involving oxygen which seems to have been published is the rose center (*7*). It consists of the molecular ion $(YO_2M)^{2+}$ with M = Ca, Sr, Ba. Its model is shown in Fig. 1. The center was identified and its structure was determined by EPR and ENDOR techniques (*7*). A Raman investigation (*8*) resolved a structural ambiguity which could not be settled with EPR.

During our experimental investigation we found that a set of similar centers is obtained when yttrium is replaced by one of the elements Sc, Lu, Ho. This paper presents these centers and some results regarding their preparation. The underlying investigation was performed essentially with Raman spectroscopy and occasionally with EPR. All of these centers possess a relatively broad adsorption band in the visible and it turned out that Raman spectroscopy is ideally suited to investigate them because they could be studied under resonant conditions with respect to this absorption band.

This type of study might be applicable to other diffusion reaction processes in solid-state sciences.

In the next section we describe the exper-

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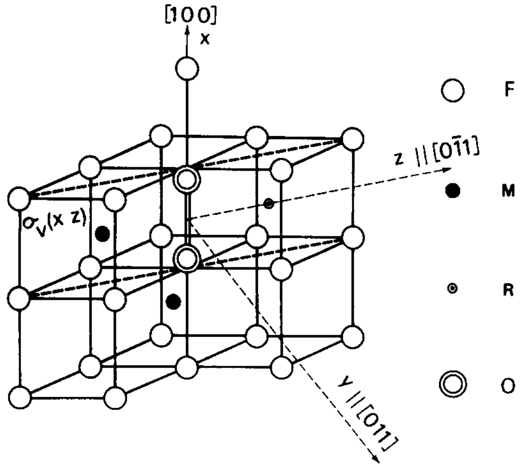

FIG. 1. Model of the $(RO_2M)^{2+}$ center in the fluorite-type crystals. Its symmetry is C_{2v}.

imental procedures. Then, the results gathered on the hydrolysis process are presented, and in the last section we give the Raman results obtained for the new analogs of the rose center.

Experimental Production of the Centers

Single crystals of the three alkaline earth fluorides were grown in a Bridgman-type furnace. This apparatus consists of two concentric, vertically mounted quartz tubes sealed at one end and connected at the other end to the high-vacuum port of a diffusion pump through a liquid nitrogen trap. Cooling water is circulated between the two tubes. The starting material contained in a graphite crucible is placed into the inner tube and is molten under high vacuum ($<10^{-6}$ Torr) with the aid of a mobile RF coil located on the outside of the tubes. The graphite crucibles were made of highest-purity graphite (quality: "nuclear purity" before 1967 and "pureté totale" after this date).

This procedure yields perfectly transparent and oxygen-free crystals. Even very small leaks in the sample chamber result in opaque crystals which show precipitation. For this reason extreme care was taken in obtaining a very good vacuum in the quartz cylinder. Useable crystals were also obtained when CaO is added to the melt contained in a vitrified graphite crucible under otherwise identical conditions. Alkaline earth fluoride salts were of ultrapure quality (Merck, Darmstadt, BRD) or optran quality (from BDH, England). The metals Sc, Y, La, Lu and the rare earths (respectively their fluorides) were from Fluka or Johnson Mathey. Their purity was 99.9% or better. The impurity cations were directly added to the melt with a small quantity of PbF_2. The quality of the obtained crystals depends strongly on the nature and the concentration of the impurity cation added. At a given impurity concentration (investigated for most systems at a concentration of 0.5% or below) the quality of the single crystals diminishes in the direction $CaF_2 \rightarrow BaF_2$. Bad crystals were heavily strained with large mosaic angles (5 to 10°). Comparing the sequence of cations Sc^{3+}, Y^{3+}, La^{3+}, Lu^{3+}, Ho^{3+} in a given host we observed the behavior collected in Table I. Sc^{3+} seems to produce the most strained crystals, and regarding the host BaF_2 it is probably best introduced by diffusion (*9*), although the obtained concentrations are small in this case.

A remarkable, albeit known, result is that yttrium enters relatively easily into these hosts, especially into CaF_2, where concentrations of 10% are obtained without special difficulties.

The fact that the as-grown crystals are free of oxygen has been tested repeatedly with EPR. Indeed, when these crystals contain oxygen they exhibit, after X-raying, the centers discussed below. The useable samples never exhibited these signals. The as-grown crystals are all colorless. The oxygen was introduced into the as-grown samples with the aid of the hydrolysis reaction. Two experimental techniques were used depending on the concentration of oxygen one

TABLE I

Optical Properties of the $MF_2:R^{3+}$ Crystals at Several Stages of the Treatments Described in the Text

	$CaF_2:Sc^{3+}$	$CaF_2:Y^{3+}$	$CaF_2:Lu^{3+}$	$CaF_2:Ho^{3+}$	$SrF_2:Sc^{3+}$	$SrF_2:Y^{3+}$	$SrF_2:Lu^{3+}$	$BaF_2:Y^{3+}$
Crystal irradiated but unhydrolyzed	Yellow	Blue-violet	Yellow-orange	Clear brown	Blue-violet	Green	Rose-mauve	Colorless
Crystal hydrolyzed and irradiated	Whitish yellow	Rose	Orange-red	Red-rose	Rose	Rose	Rose	Red
Position of the maximum of the corresponding absorption band (nm)	437	486	455	500	480	510	485	535

Note. The $BaF_2:Sc^{3+}$ crystals, not mentioned in the table, were unuseable and the $SrF_2:Sc^{3+}$ ones just useable. All of the other systems gave useful crystals of quality which decreases from Y^{3+} to La^{3+} as a function of the impurity and which decreases as a function of the host lattice from CaF_2 to BaF_2.

wanted to introduce into the sample. In the strong hydrolysis situation the sample was placed into a quartz tube at the center of a cylindrical furnace. One end of the tube was connected to a water jet pump and the other extreme connected to a glass vessel containing a few cubic centimeters of distilled water. The crystal was heated to approximately 900°C during the desired time, while the water jet pump was constantly pumping. The resulting samples were whitish and opaque after this treatment. The strongly hydrolyzed ones became deliquescent.

In the situation termed as weak hydrolysis the crystal is introduced into a quartz ampoule which is evacuated with a water jet pump. Then, the tube is sealed off. Occasionally the tubes were evacuated with a diffusion pump. The ampoule is then heated for several hours to 900°C. The water vapor and/or the $(OH)^-$ groups freed at high temperatures by the quartz walls produce the desired hydrolysis reaction. The crystals show reduced transparency with respect to the untreated samples and they present some opalescence in a strong white light beam.

After the strong or the weak hydrolysis treatment, respectively, the samples did not show any EPR signal related to the centers discussed in this paper. But it is sufficient to irradiate them with X rays for a few hours in order to produce several centers and to obtain strongly colored crystals. The ESR experiments were performed on a Varian V-4500 X-band apparatus. The ENDOR spectrometer consisted of a laboratory-built attachment to this spectrometer. The Raman equipment is laboratory assembled around a Spectra Physics Ar ion laser (Model 166), a Spex 14018 double monochromator, and an Ortec photo counting system (5C1). The samples were X-rayed either with a laboratory-assembled generator or with Philips (Type PW2184) equipment. Both apparatus contained a W anticathode tube. Typical working conditions were 40 kV/30 to 40 mA.

Hydrolysis

Many of our investigations on the mechanism of formation of the centers during hydrolysis were realized on the system $CaF_2:Y$ and on pure CaF_2 crystals. The other impurity cations yield for the most part similar results when the appropriate times of treatment are applied. Weakly hydrolyzed pure CaF_2 samples showed after X-raying the O^- (*10*) and the $(OF)^{2-}$ (*11*) centers. Figure 2a represents the (normalized) concentration of the two centers as a function of the irradiation time. In addition to these centers we observed very often the rather weak EPR spectrum of the atomic hydrogen center (*12*).

Several crystals were heated for 30 min to 250°C after they had been treated as described above. Then, they were again X-rayed. The important result is that after this treatment the density of the $(OF)^{2-}$ centers increased strongly, whereas the concentration of the O^- is only about 20% of the value observed after the first treatment run. It is well known that, globally speaking, the hydrolysis reaction produces oxygen ions which diffuse into the lattice. Our experiments show that some of these are O^{2-} ions on anion lattice sites in an otherwise unmodified surrounding. Prolonged X-raying converts part of these centers into $(OF)^{2-}$ structures by knocking off an F^- neighbor of the oxygen. Indeed, the $(OF)^{2-}$ center has a fluorine vacancy associated with the oxygen ion.

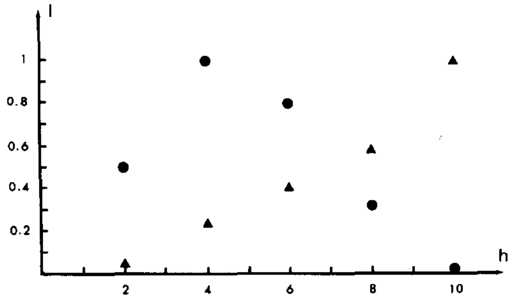

FIG. 2a. Concentration of the O^- center (●) and of the $(OF)^{2-}$ center (▲) as a function of the X irradiation time. The intensities were normalized to the strongest spectrum of each species. The measurements were performed by EPR at X-band frequency. Temperature of measurement was ≃6K.

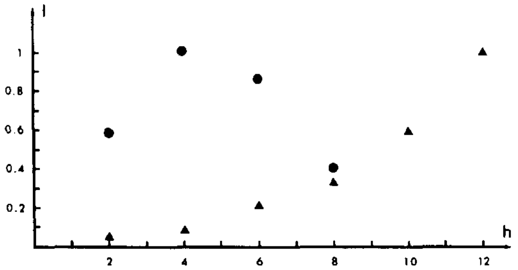

FIG. 2b. The concentration dependence of $(OF_2Y)^+$ center (●) and $(YO_2Ca)^{2+}$ center (▲) on the duration of the hydrolysis. The experimental conditions are the same as those given in Fig. 2a.

Another interesting result of these experiments is the presence of the H^0 in the lattice. This observation directly evidences one step in the reaction mechanism which was postulated a long time ago (*2*). It is known from the work of Bontinck that the hydrolysis reaction creates at the surfaces of the crystal $(OH)^-$ and the HF species. In our reaction the HF molecules react with the wall of the quartz ampoule (which becomes opaque) in the weak hydrolysis case and they are eliminated by the water jet pump in the strong hydrolysis case. But part of the $(OH)^-$ definitely diffuses into the crystals. At some time during the diffusion process the $(OH)^-$ dissociates and the hydrogen seems to form weak bonds with the F^- ions in the lattice. The X-raying process changes the charge state of the hydrogen. Probably, it traps an electron liberated from the $(OF_2Y)^+$ center and the $(RO_2M)^{2+}$. The possibility that during the hydrolysis free hydrogen might be present is virtually nonexistent because of the strongly oxidizing conditions.

An interesting experimental fact is that pure CaF_2 crystals are much less easily hydrolyzed than the ones doped with a trivalent cationic impurity. Typically the time of the treatment has to be larger by a factor of 3 to obtain a center concentration comparable to the one observed in $CaF_2 : Y^{3+}$. The weakly hydrolyzed $CaF_2 : Y^{3+}$ samples show the $(OF_2Y)^+$ center in addition to the O^- and the $(OF)^{2-}$ centers. It is largely dominant with respect to the two last-mentioned centers (a typical ratio is 5 : 1 to 20 : 1 in a crystal containing 0.5 to 1% of Y^{3+} ions). The H^0 center was always weak or absent. Under strong hydrolysis conditions essentially the centers $(OF_2Y)^+$ and $(YO_2Ca)^{2+}$ are observed. Figure 2b shows the observed concentrations as a function of the duration of the hydrolysis reaction. Short treatment times produce essentially the $(OF_2Y)^+$ which involves one oxygen ion. Increasing the hydrolysis reaction time produces a steadily growing oxygen concentration in the crystal and the $(OF_2Y)^+$ centers trap a second oxygen ion. In addition to these two centers the ESR spectrum of H^0 having comparable intensity was always present. But it is not stable and after the crystal had been for a few weeks in the drawer at room temperature the spectrum was no longer observed.

The paper by Catlow (*6*) analyzes the hydrolyzation mechanism with the aid of an extended Born model. With the aid of the HARWELL Hades lattice dynamics program Catlow calculates, among other things, the energy and enthalpy of several possible oxygen complexes. His results are suitable for a qualitative comparison with our experiments.

The paper predicts an energy of +1.55 eV for the hydrolyzation reaction and +4.7 eV for the oxidation process. These figures include the lattice defect energies and are calculated for CaF_2. Similar results are given for the other two hosts. These results confirm the experimental finding that the hydrolysis reaction (although also exothermic) is energetically more favorable than the oxidation reaction. Additional calculations show that the hydrolysis reaction is energetically even more favorable when the crystals contain R^{3+} ions. One essential reason is that the charge compensation of the R^{3+} ion by an O^{2-} yields a total energy which is lower by typically 15 eV as compared to the energy gained by a substitutional F^- ion. The easiness with which the $(OF_2Y)^+$ and the $(RO_2M)^{2+}$ are formed strongly supports these results.

The general picture is similar for Y^{3+} in SrF_2. In BaF_2 only some of these centers have been observed. In addition the hydrolyzation times necessary to produce similar effects are longer by approximately 50%. The other impurities exhibit similar results except the La^{3+} in the three matrices and Sc^{3+} and Lu^{3+} in BaF_2. The two last-mentioned ones were problematic with respect to crystal growth, whereas the La^{3+} behaves like Sm, Eu, Gd, Yb, Tm, where under the hydrolysis conditions described above no O_2^{3-} structure was obtained.

The ($R^{3+}O_2^{3-}M^{2+}$) Centers

This section focuses on the identification and spectroscopic properties of the analogs of the $(YO_2Ca)^{2+}$ center.

The coloration observed and the position of the corresponding absorption band of the strongly hydrolyzed crystals are presented in Table I. Previous papers (*7, 8*) demonstrated that the coloration of the $CaF_2 : Y + O$ system is due to the rose center and that the resonant Raman spectrum observed with respect to this absorption band is also due to this center.

This Raman investigation was extended to all of the systems listed in Table II. Raman spectra are observed which are very similar to that of the rose center. They consist of a broad band at a frequency situated between 70 and 150 cm^{-1}, depending on the

TABLE II

POSITIONS OF THE RAMAN LINES OF THE $MF_2:(RO_2M)^{2+}$ SYSTEMS

	T (K)	Acoustic band	T_{2g}	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$	$\tilde{\nu}_1 + \tilde{\nu}_2$	$2\tilde{\nu}_2$	$\tilde{\nu}_3 + \tilde{\nu}_2$
$CaF_2:(ScO_2Ca)^{2+}$	Room	157	323	364	429	595			
	78	165	327	368	437	597	733	819	995
				(10)	(53)	(31)			
$CaF_2:(YO_2Ca)^{2+}$	Room	155	323	361	411	534			
	78	165	327	364	415	537			
				(19)	(74)	(34)			
$CaF_2:(LuO_2Ca)^{2+}$	Room	150	323	358	411	530			
	78	155	327	361	416	533			
					(72)	(47)			
$CaF_2:(HoO_2Ca)^{2+}$	Room	160	325	364	413	536			
$SrF_2:(ScO_2Sr)^{2+}$	Room	—	286	318	405	583			
	78	111	289	328	412	588			
					(16)	(19)			
$SrF_2:(YO_2Sr)^{2+}$	Room	108	286	315	386	516			
	78	113	289	319	390	513			
				(19)	(31)	(42)			
$SrF_2:(LuO_2Sr)^{2+}$	Room	100	283	314	390	510			
	78	106	289	318	391	508	712	779	900
				(20)	(27)	(46)			
$BaF_2:(YO_2Ba)^{2+}$	Room	73	243	278	358	487			
	78	76	248	280	361	481	1000	1078	1198
				(14)	(18)	(20)	(27)	(35)	(37)

Note. The precision of the measurements is ±3 cm^{-1}. Linewidths are given (when possible) in brackets below the corresponding line position. Their precision is ±5 cm^{-1}.

system observed, and of three lines beyond the T_{2g} Raman transition which is due to the host lattice. The position and width of the three lines depend somewhat on the host and quite strongly on the impurity and on the oxygen isotope. Polarization experiments realized on these lines (the details are found in the captions of the relevant figures) showed that they always have the same polarization properties. We demonstrated previously that this polarization behavior implies a totally symmetric (A_1) polarizability tensor of the individual center. The structure of these tensors, written in the local axes (C_{2v} symmetry), is

$$\mathbf{P}(A_1) = \begin{pmatrix} a & & \\ & b & \\ & & c \end{pmatrix}.$$

Figures 3, 4, and 5 present Raman spectra of several of the observed systems and Figs. 6a, b, and c give the polarization dependence of these lines. These spectra and the table in (*8*) easily enable one to verify the structure of the polarizability tensor of the individual center. A more detailed discussion of the polarization investigation is given in (*8*).

The similarity of the Raman spectra of all the systems listed in Table II indicates that the $(RO_2M)^{2+}$ structure is present in the crystals and is at the origin of the optical spectra obtained.

Additional support for the identification is obtained from EPR measurements performed on all of the yttrium systems, on the Sc centers, the Ho center, and, in part only, on the Lu center (study in progress). All of these centers show the specific EPR spectrum detected first on $(YO_2Ca)^{2+}$.

Once the origin of the observed Raman spectra had been settled, their structure could be interpreted in more detail. The free $(RO_2M)^{2+}$ entity involves the genuine vibrations $3A_1 + 2B_1 + B_2$ (in the axes of Fig. 1).

The three lines at a frequency higher than that of the T_{2g} line are due to the pseudolocalized inner vibrations of the molecular cluster. The polarization experiments show that they are of A_1 symmetry. It is remarkable to compare their widths at a given temperature as a function of the system (Table II). The experiments show that the combination of a heavy host cation together with a light metallic impurity gives the smallest linewidths, whereas the combination of a light host cation and heavy impurity yields rather broad Raman lines. The heavier the host cation the lower the high-frequency cutoff of the crystal phonon spectrum. The frequencies of the localized vibrations of the $(RO_2M)^{2+}$ center depend, on the other hand, critically on the mass of the impurity cation. The quantity (frequency of a given

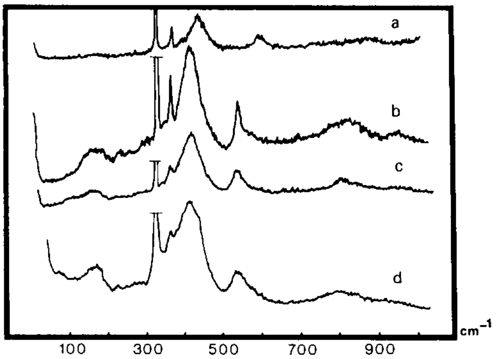

FIG. 3. Raman spectra and the associated experimental conditions of the following systems: (a) $CaF_2:(ScO_2Ca)^{2+}$, $\lambda = 457.9$ nm (0.2 W), $T = 78$K; (b) $CaF_2:(YO_2Ca)^{2+}$, $\lambda = 488$ nm (0.4 W), $T = 78$K: (c) $CaF_2:(LuO_2Ca)^{2+}$, $\lambda = 488$ nm (0.3 W), $T = 78$K; (d) $CaF_2:(HoO_2Ca)^{2+}$, $\lambda = 488$ nm (0.35 W), $T = 293$K. The resolution is 3.5 cm^{-1}.

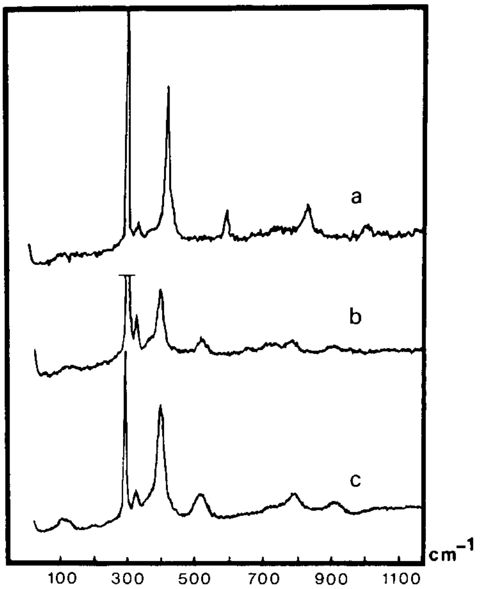

FIG. 4. Raman spectra of the $SrF_2:(RO_2Sr)^{2+}$ systems. (a) $SrF_2:(ScO_2Sr)^{2+}$; (b) $SrF_2:(YO_2Sr)^{2+}$; (c) $SrF_2:(LuO_2Sr)^{2+}$. The experimental conditions were the following: $\lambda = 488$ nm, $T = 78$K, and the resolution $= 4$ cm^{-1}. The laser powers were 0.2 W (a), 0.6 W (b), and 0.3 W (c).

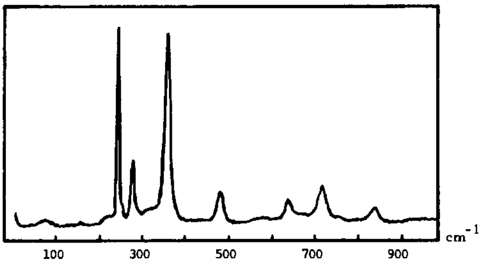

FIG. 5. Raman spectra of a $BaF_2:(YO_2Ba)^{2+}$ monocrystal. $\lambda = 514.5$ nm (0.6 W), $T = 78$K, resolution $= 4$ cm^{-1}.

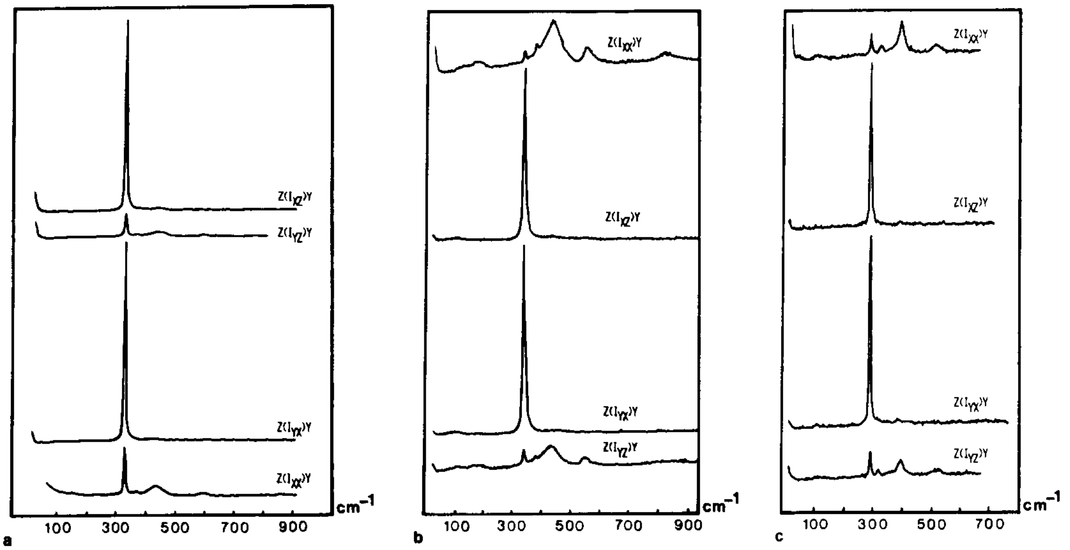

FIG. 6. Polarization properties of the centers with respect to the frame of the crystal defined in Fig. 1. (a): $CaF_2:(ScO_2Ca)^{2+}$, laser power 0.2 W. (b): $CaF_2:(LuO_2Ca)^{2+}$, laser power 0.3 W. (c): $SrF_2:(LuO_2Sr)^{2+}$, laser power 0.3 W. The following parameters are common to all three: $T = 78$ K, $\lambda = 488$ nm, resolution = 4 cm^{-1}.

cluster mode-cutoff frequency of the phonon spectrum) can be used as an approximate criterion to classify the cluster vibrations either as in-band or as pseudolocalized ones.

The system $CaF_2:Y$ implies essentially in-band vibrations with broad associated Raman lines. The $BaF_2:Y$ and the $SrF_2:Sc$, $CaF_2:Sc$ systems correspond to quite strongly localized vibrations. Overtones and combination vibrations are observed in the spectra of these centers (especially beautifully with $BaF_2:(YO_2Ba)^{2+}$, see Fig. 5).

Conclusions

We have shown in this paper that strong hydrolysis of alkaline earth fluorides doped with the impurities Sc, Y, Lu, Ho yields a set of centers of the type $(RO_2M)^{2+}$ and of the structure as shown in Fig. 1. The only systems where this center could not be obtained are $BaF_2:R^{3+}$ (R = Sc, La, Lu) and $MF_2:La^{3+}$ (M = Ca, Sr, Ba).

Raman spectroscopy is a particularly appropriate tool for the investigation of these centers, in part because the signal-to-noise ratio is strongly enhanced by the resonant Raman effect.

Several of the identified centers were also investigated with EPR and the correlation of these results with those obtained from the Raman experiments gives additional support for their identification.

The investigation on these centers yields information on the hydrolysis reaction and seems to show that to a large extent geometrical criteria determine the possible centers. Indeed, if the impurity cation is too large compared to the host cation the crystal growth is perturbed and, in addition, the $(RO_2M)^{2+}$ centers cannot be formed because the O^{2-} are not sufficiently close together. Let us recall, for example, that $SrF_2:La^{3+}$ did not show any $(LaO_2Sr)^{2+}$ center but that after hydrolysis we observed the O^- center (*13*). Therefore, the oxygen enters but does not easily associate. A remarkable fact should be pointed out. Alkaline earth fluorides doped with the *RE* ions Sm, Eu, Gd, Tm, Yb, Er show only the influence of a crystal field modified by oxygen neighbors on the *f* electrons, whereas the impurities reported in this paper yield, after hydrolysis, a new type of center. In it the magnetic electron is essentially located on the oxygens associated with the impurity metal.

Acknowledgments

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