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COLOUR CENTRES AND POINT DEFECTS IN IRRADIATED CALCIUM FLUORIDE

by

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Chalk River Nuclear Laboratories
Chalk River, Ontario
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ABSTRACT

The optical absorbance of single crystals of pure CaF_2 and CaF_2 doped with NaF and YF_3 was measured before and after ^{60}Co gamma irradiation and 18 MeV proton irradiation at 20°C and -196°C. Selected specimens were subsequently annealed at various temperatures up to 300°C.

The pure crystals were unaffected by irradiation; however, the Na-doped crystals developed prominent bands at 429, 386 and 316 nm after -196°C irradiation and at 609, 495, 386 and 333 nm after 20°C irradiation. On annealing, the -196°C spectrum was first converted into that for 20°C irradiation. New bands then appeared at 530 and 561 nm as a final stage in the decay of the spectrum.

For the Y-doped crystals the main bands were at 586, 512, 333, 313 and 269 nm for -196°C irradiation and at 512, 392, 358, 313 and 245 nm for 20°C irradiation. No new bands were detected on heating above 20°C. Numerous lesser bands have been identified for both specimen types.

Certain of the major bands have been tentatively attributed to particular defect centres.

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Centres de couleurs et défauts ponctuels dans du fluorure de calcium irradié

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Résumé

L'absorption optique de monocristaux en CaF_2 pur et en CaF_2 dopé de NaF et de YF_3 a été mesurée avant et après une irradiation gamma au ^{60}Co et une irradiation protonique de 18 MeV, à 20°C et à -196°C. Certains spécimens ont été subséquemment recuits à des températures allant jusqu'à 300°C.

Les cristaux purs n'ont pas été altérés par l'irradiation; cependant, les cristaux dopés de Na ont donné des bandes proéminentes à 429, 386 et 333 nm après irradiation à -196°C et à 609, 495, 386 et 333 nm après irradiation à 20°C. Lors du recuit, le spectre à -196°C a d'abord été converti en celui de l'irradiation à 20°C. De nouvelles bandes sont alors apparues à 530 et 561 nm, comme stade final de la décroissance du spectre.

Pour les cristaux dopés de Y, les bandes principales étaient à 586, 512, 333, 313 et 269 nm pour l'irradiation à -196°C et à 512, 392, 358, 313 et 245 nm pour l'irradiation à 20°C. Aucune nouvelle bande n'a été détectée lors du chauffage à plus de 20°C. De nombreuses bandes moins importantes ont été identifiées pour les deux types de spécimens.

Certaines des bandes majeures ont été provisoirement attribuées à certains défauts cristallins.

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INTRODUCTION

The work to be described forms part of a more general study of point defect characteristics and defect-impurity interaction effects in a class of technologically important materials, including UO_2 and ThO_2, which have the calcium fluoride structure and predominantly ionic bonding. Calcium fluoride itself is of particular interest in this connection since it is readily available in single crystal form both in a highly pure state and, also, doped with various selected impurities. Furthermore, the material has been extensively investigated in the past so that a great deal of information is available to support further studies.

This paper is concerned with the behaviour of the optical absorption bands for pure and doped calcium fluoride crystals following irradiation at 20°C and -196°C and subsequent annealing.

EXPERIMENTAL

The specimen material used was of 3 types:

1) highly pure crystals*
2) crystals doped with 0.1 mol% NaF†
3) crystals similar to (1) but doped with 0.34 mol% YF_3

Sodium and yttrium doping of calcium fluoride have been shown(1,2) to result in the introduction of fluorine vacancies and interstitials respectively into the lattice for charge compensation. These defects, in the equilibrium condition, are believed to be closely associated with the corresponding impurity ion except, perhaps, at high temperatures.

Polished wafers 0.1 - 1.0 mm thick, prepared from the crystals, were irradiated at 20°C and -196°C by a ^{60}Co gamma source or an 18 MeV proton beam. The respective exposures ranged up to about 5×10^7 r and 3×10^{15} protons incident on the area of the specimen under study.

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*Harshaw Chemical Company, Solon, Ohio. Typical impurity levels reported to be 3 ppm Al, 3 ppm Mg, 2 ppm Si.

†Isomet Corporation, Oakland, N.J. Typical impurity levels reported to be 50 ppm Sr, 10 ppm Fe, 5 ppm Si.

The optical absorbance of the specimens was measured* at the irradiation temperatures before and after exposure and also after anneals in vacuum or air at temperatures up to 300°C. The 3 chart traces from the spectrophotometer corresponding to the total wavelength range of about 210-2700 nm were mechanically digitized and the output computer-processed to provide a single normalized spectrum corrected for instrumental and specimen background effects. The spectrum for each specimen was resolved† into component bands, corresponding to the absorption at various defect and impurity centres. The shapes of individual bands in many cases were asymmetric and approximated to skew Gaussian functions.

The resolution procedure adopted was based on the assumptions

(a) that a unique set of bands exists for each material, the bands having characteristic forms, mean energies and mean widths,

(b) that the variability in energy and width for a given band is the same for all specimens: thus values obtained for spectra in which the band is free from serious overlap by adjacent bands can be applied to cases where overlap occurs,

(c) that similar specimens treated in a similar way will exhibit the same sub-set of bands,

(d) that a given spectrum should be resolved into the minimum number of bands necessary to produce a satisfactory fit within the experimental accuracy of the data.

The set of bands for each material was determined by examining the spectra of many similar specimens subjected to a variety of treatments. Particular treatment conditions resulted in individual bands becoming relatively prominent and clearly identifiable - particularly when these were present

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* with a Perkin-Elmer model 450 spectrophotometer calibrated relative to the holmium oxide spectrum(3).

† with a Dupont Instrument Corp. model 310 curve resolver.

for a number of specimens. This procedure, of course, results in a minimum set of bands characteristic of the particular range of conditions studied. Within this range, however, it is unlikely that many bands remain undetected in view of the many specimen-treatment combinations employed.

RESULTS

The pure specimens irradiated at 20°C to the maximum gamma or proton exposures showed no intrinsic absorption bands. Some of the specimens developed traces of the well-known four-band spectrum first observed by Smakula(4) and later attributed(5) to the presence of yttrium impurity.

Similar specimens irradiated (2.0×10^6 r) and measured at -196°C also showed no intrinsic bands contrary to the observation of Tanton and co-workers(6) who observed the F band at 375 nm after irradiation to 8×10^5 r.

Sodium-doped CaF_2 specimens, which also showed no absorption bands initially, gave spectra similar to those in Figs. 1(a) and (b) for gamma exposures of 2.4×10^4 and 8.4×10^4 r respectively at -196°C. These spectra could be resolved into three prominent bands, labelled S_η, S_κ and S_λ, at 316, 386 and 429 nm respectively. In addition, the presence of three lesser, overlapping, bands at 254 nm (S_γ), 278 (S_ε) and 353 nm (S_ι) was inferred using the procedure described above.

Specimens gamma-irradiated and measured at 20°C showed still more complex spectra (Figs. 1(d) and (e) for 6.0×10^4 and 1.2×10^5 r respectively) with a number of additional bands developing around a particularly prominent band (S_ρ) at 609 nm. Typical of these were small bands at 495 nm (S_μ) and 675 nm (S_σ). Further bands were also produced in the ultra-violet region - in particular at 247 nm ($S_{\gamma'}$) 265 nm (S_δ), 298 nm ($S_{\eta'}$) and 333 nm (S_θ). In contrast, the S_λ band, relatively prominent on irradiation at -196°C, was very small or absent for irradiation at 20°C.

Similar spectra were also obtained following gamma-irradiation at -196°C and measurement at 20°C. No significant shift in band heights or positions occurred on cooling from 20°C to -196°C.

Proton irradiation, using a liquid-nitrogen cooled target, resulted in spectra at -196°C (e.g. Fig. 1(c) for 10^{12} incident protons) intermediate in character between the -196° and 20°C gamma irradiation spectra. Thus, both the S_{ρ} band, characteristic of 20°C irradiation, and the S_{λ} band, characteristic of -196°C irradiation, were present. The heating effect of the proton beam was probably responsible for this, the actual specimen temperature being raised somewhat above that of the target block.

A further apparent difference between the gamma and proton-irradiated specimens was the appearance of small bands at 215 nm ($S_{\alpha'}$), 220 nm (S_{α}), 228 nm ($S_{\beta'}$), 238nm(S_{β}), 288 nm (S_{ζ}), 737 nm (S_{τ}), 835 nm (S_{ϕ}) and 928 nm (S_{χ}). The extent to which the formation of these bands is unique to proton irradiation is not known at present.

Specimens annealed in vacuum or air at temperatures above 20°C developed some new bands while existing bands decreased in area or disappeared. Figure 2 shows spectra for two relatively highly irradiated specimens (4.6 x 10^{14} and 4.8 x 10^{14} incident protons) which were subsequently annealed in air for 10 min at 135°C and 200°C respectively. Major bands grew in at 530 nm (S_{ν}) and 561 nm (S_{π}) under these conditions whereas the S_{κ} band, initially the major one, virtually disappeared. Other, lesser, bands developed on annealing, at 404 nm ($S_{\lambda'}$), 453 nm ($S_{\mu'}$) and 1160 nm (S_{ω}) while another band, most probably a new one, appeared at the S_{λ} band wavelength. No significant difference has been observed between the spectra of specimens annealed in air and those annealed in vacuum so it seems unlikely that the S_{ν} and S_{π} bands, in particular, involve diffused oxygen centres.

The temperature dependence of the areas of the main bands for typical specimens and irradiation conditions is summarized schematically in Fig. 3. The detailed features of this behaviour varied slightly over the range of conditions covered. In particular, the S_κ band tended to anneal out at lower temperatures as the radiation exposure increased.

A list of the bands positively identified for CaF_2:NaF is given in Table I.

The yttrium-doped specimens, also initially free from absorption bands, gave spectra similar to those shown in Fig. 4(a) and (b) following gamma irradiation at -196°C (6.0×10^4 and 1.2×10^5 r respectively). Intercomparison of the data for all specimens showed that these spectra were composed of at least 5 major bands at 269 nm (Y_δ), 313 nm ($Y_{\zeta'}$), 333 nm (Y_ζ), 512 nm (Y_κ) and 586 nm (Y_λ). A number of lesser bands were also present for many of the specimens at 237 nm ($Y_{\beta'}$), 777 nm (Y_ν) and 861 nm (Y_π).

Gamma irradiation at 20°C resulted in quite different spectra (Fig. 4(c) and (d)). The Y_δ, Y_κ and $Y_{\zeta'}$ bands were greatly reduced or absent while major new bands were produced at 358 nm (Y_η), 392 nm (Y_θ) and 418 nm ($Y_{\iota'}$). Other large bands were formed at 228 nm (Y_α) and 245 nm (Y_β) together with a number of lesser bands as listed in Table II.

Proton irradiation resulted in similar spectra except that most of the specimens irradiated, using the liquid nitrogen-cooled target, gave spectra at -196°C corresponding more to those for 20°C gamma irradiation. Again, this was most probably due to the heating effect of the beam.

As in the case of the sodium doped specimens, the spectrum corresponding to 20°C irradiation could be obtained by irradiating at -196°C and heating at 20°C for 1 hr. Again no significant change in band positions or widths for this spectrum occurred on cooling from 20°C to -196°C.

The annealing behaviour of the bands up to 200°C, with measurement at -196°C, is indicated schematically in Fig. 5. From the behaviour of the proton-irradiated specimens, the Y_θ

and Y_η band areas appear to pass through a maximum at some temperature between -196°C and 20°C while the Y_ι' band peaks near 20°C and the Y_β band near 100°C. The Y_λ band appears to be the most stable of the bands produced at -196°C. All the bands disappeared following a final anneal at 300°C.

DISCUSSION

Previously reported data(7,8,9) for absorption band wavelengths of irradiated CaF_2:NaF crystals, summarized in Table III agree well with our values - at least for the prominent S_η, S_λ, S_μ and S_ρ bands. Most of the other bands reported here have not been observed, apparently, by other workers. This may be due mainly to our use of a large number of specimen-treatment combinations thus increasing the probability that individual bands will be identified and resolved.

The most similar study to ours, that of Scouler and Smakula(9), was performed on CaF_2 crystals doped with 0.07 mole% NaF and irradiated with 2.5 MeV electrons at 20°C and -190°C. The disappearance of the S_λ band and the formation of the S_ρ and S_μ bands on heating from -190°C to 20°C were noted; however the formation of the S_ν and S_π bands on annealing at higher temperatures was not observed.

Despite the high concentration of anion vacancies in these doped crystals it seems unlikely that any of the bands observed corresponds to the true F band. This has been well established(10,11) to occur at 375 nm. It is very possible, however, that the S_κ band at 386 nm corresponds to an F centre perturbed by association with a Na ion. A similar band at about the same wavelength has been observed(12,13) for H-doped CaF_2 irradiated at -196°C, and supporting EPR and Faraday rotation measurements leave little doubt that this is a perturbed F band.

Furthermore, this band is accompanied by a satellite at about 440 nm which also has the characteristics of a perturbed F band and appears very similar to our S_λ band. On annealing the CaF_2:H specimens above -160°C, the original two bands disappeared and were replaced by new bands at 366 nm and 565 nm the latter strongly resembling our S_ρ band and attributed to a perturbed M centre.

We thus suggest that both the S_κ and S_λ bands probably result from perturbed F centres, the anion vacancy possibly being in the nearest neighbour position to the Na ion for the S_κ centre and in the next nearest neighbour position (1 of 24 equivalent sites) for the S_λ centre. This latter identification is consistent with the observation that the S_λ band is thermally unstable compared to the S_κ band and with the expectation that some anion vacancy - Na ion pairs may be partially dissociated on ionization.

The complete dissociation of these centres, on annealing, and the subsequent diffusion of the isolated F centres to combine with other perturbed F centres or anion vacancy - Na ion pairs would then result in the formation of perturbed M centres. Identification of the S_ρ band with a perturbed M centre is thus also consistent with the proposed model.

Turning now to the $CaF_2:YF_3$ system, our values for the principal band wavelengths again agree well with the earlier data(9,14,15,16) (Table IV). The 4 bands of the Smakula(4) spectrum are those labelled Y_α, $Y_\zeta/Y_{\zeta'}$, Y_θ and Y_λ. Again, the larger number of bands reported here results from the use of the techniques described as opposed to the normal practice of reporting only gross features of unresolved spectra. Measurements following irradiation at both -196° and 20°C have been made by two groups. Scouler and Smakula(9), using specimens irradiated at -190°C with 2.5 MeV electrons, noted the appearance of the Y_θ band and disappearance of the Y_δ band on heating. However, in contrast to our observations, they interpreted the behaviour of the Y_ζ, $Y_{\zeta'}$ and Y_κ , Y_λ pairs of bands in terms of a shift in wavelength of single composite bands rather than as a relative change in amplitude of one of two fixed wavelength components. Our conclusion is based on spectra which clearly contain more than one component in these composite bands. Further confirmation has come from recent preliminary experiments(17) in which the absorption has been measured first as a function of increasing exposure and then of increasing temperature. Similar observations of apparent band shifts were made by O'Connor and Chen(15). In both investigations a corresponding apparent change in shape of the composite $Y_\zeta/Y_{\zeta'}$ band also occurred. This is consistent more with a composite than a single band model.

It appears from O'Connor and Chen's work(5) that electron centres must be responsible for at least the major bands in the $CaF_2:YF_3$ system. They observed that introducing competing electron traps such as Sm^{3+} completely suppressed the absorption spectrum. This, of course, would eliminate F° interstitials as possible centres. Theissing et al.(14) have shown, contrary to earlier statements(15), that only one of the main bands, most probably the Y_λ, can be due to isolated Y^{2+} ions. The others most likely involve various combinations of Y ions and F interstitials. The formation of the Y_θ, Y_η and $Y_{\iota'}$ bands, on heating, very possibly involves the decomposition of some such compound centres coupled with the diffusion of F interstitials to more stable positions adjacent to other types of centre. Hole transfer alone as a possible mechanism for the formation of these bands, seems unlikely for the reason given above.

Two further possible centres have been identified(16) by EPR and ENDOR techniques in $CaF_2:YF_3$ specimens containing oxygen as an impurity. The more stable of these - a $(YO_2)^\circ$ molecule with a corresponding band at 486 nm - is believed to form by hole transfer from previously ionized (Y-O) centres at around 100-150°C. It is unlikely that any of our bands is due to the $(YO_2)^\circ$ centre since the wavelengths and formation kinetics do not agree. It is possible, however, that one or more types of (Y-O) centre may occur in our specimens and give rise to some of the lesser bands.

CONCLUSIONS

Irradiation of sodium or yttrium-doped calcium fluoride at -196°C or 20°C, followed by annealing at temperatures up to 300°C, results in various characteristic and complex absorption spectra. By using a sufficiently large number of specimens and treatment conditions and with some simple and reasonable assumptions it is possible to resolve these spectra into individual absorption bands as listed in Tables I and II.

Several of these bands are reported here for the first time.

In some cases extra bands have been observed for proton-irradiated over those for gamma-irradiated specimens. Further work is required to substantiate this.

For both types of specimen, irradiation at 20°C produced similar spectra to irradiation at -196°C followed by annealing at 20°C. Also, we have observed no significant shift in band wavelengths on cooling from 20°C to -196°C.

Annealing specimens after irradiation at - 196°C caused some bands to disappear (S_λ for CaF_2:NaF and Y_σ, Y_κ for CaF_2:YF_3) while others were formed and grew to a maximum amplitude (S_ρ, S_μ, S_π, S_ν for CaF_2:NaF and Y_θ, Y_η, Y_ι', Y_α', Y_β for CaF_2:YF_3).

The bands cannot be positively identified with particular colour centres from the absorption measurements alone. However, on the basis of published data, it seems reasonable to equate the S_κ and S_λ bands to F centres perturbed by Na ions in nearest or next-nearest neighbour cation positions. The S_ρ band may result from a similarly perturbed M centre.

The Y_λ band seems to be due to isolated Y^{2+} ions(14) and, probably, other major bands in this spectrum (eg. Y_δ, Y_θ) to various compound (Y_{ion}-$F_{interstitial}$) centres.

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TABLE I

ABSORPTION BANDS FOR CaF_2:NaF

Band	Wavelength nm	Std. Dev. nm	Band	Wavelength nm	Std. Dev. nm
$S_{\alpha'}$	214.8	2.1	S_{κ}	385.6	3.5
S_{α}	219.7	0.9	$S_{\lambda'}$	403.6	3.3
$S_{\beta'}$	228.1	1.2	S_{λ}	428.7	4.0
S_{β}	237.8	1.1	$S_{\mu'}$	452.9	2.2
$S_{\gamma'}$	246.8	1.5	S_{μ}	495.0	3.8
S_{γ}	254.2	1.6	S_{ν}	530.3	3.7
S_{δ}	265.2	1.8	S_{π}	561.0	3.7
S_{ε}	278.1	2.8	S_{ρ}	609.0	6.7
S_{ζ}	288.1	1.5	S_{σ}	675.0	7.5
$S_{\eta'}$	298.4	1.5	S_{τ}	737.5	10.0
S_{η}	316.2	1.0	S_{ϕ}	835.5	12.0
S_{θ}	332.9	2.2	S_{χ}	928.0	15.0
S_{ι}	353.2	2.3	S_{ω}	1116.0	31.0

TABLE II

ABSORPTION BANDS FOR $CaF_2:YF_3$

Band	Wavelength nm	Std. Dev. nm	Band	Wavelength nm	Std. Dev. nm
$Y_{\alpha'}$	220.2	0.9	$Y_{\iota'}$	417.5	4.9
Y_{α}	227.6	1.4	Y_{ι}	451.4	4.9
$Y_{\beta'}$	236.5	1.5	$Y_{\kappa'}$	477.9	6.2
Y_{β}	245.1	2.2	Y_{κ}	512.3	5.7
$Y_{\gamma'}$	253.4	1.8	$Y_{\lambda'}$	537.5	10.3
Y_{γ}	259.5	1.5	Y_{λ}	586.1	6.2
Y_{δ}	268.7	2.6	$Y_{\mu'}$	645.1	9.1
$Y_{\epsilon'}$	282.7	2.3	Y_{μ}	703.3	14.2
Y_{ϵ}	293.9	3.2	Y_{ν}	777.4	7.4
$Y_{\zeta'}$	313.2	2.9	Y_{π}	860.6	11.3
Y_{ζ}	333.3	2.7	Y_{ρ}	948.5	15.1
Y_{η}	358.2	4.1	Y_{ϕ}	1069.5	21.6
Y_{θ}	392.2	2.9	Y_{χ}	1234.6	15.4

TABLE III

CaF_2:NaF ABSORPTION BANDS - COMPARISON WITH PREVIOUS DATA

Reference	Wavelengths in nm for						
		$S_{\gamma'}$	S_η	S_κ	S_λ	S_μ	S_ρ
Present	-	247	316	386	429	495	609
7		245	320	385		500	610
8				385		500	600
9	200		325	385	440		605

TABLE IV

CaF_2:YF_3 ABSORPTION BANDS - COMPARISON WITH PREVIOUS DATA

Reference	Wavelength in nm for								
	Y_α	Y_δ	$Y_{\zeta'}$	Y_ζ	Y_θ	Y_κ	$Y_{\lambda'}$	Y_λ	Y_π
Present	228	269	313	333	392	512	538	586	861
9	225	275	320 -	335	400		545 -	580	825
14	226		324		394	490		580	
15	225	276	322	335	400		547	580	828
16	226			332	396			571	

FIGURE 1 ABSORPTION SPECTRA FOR Na-DOPED CaF_2

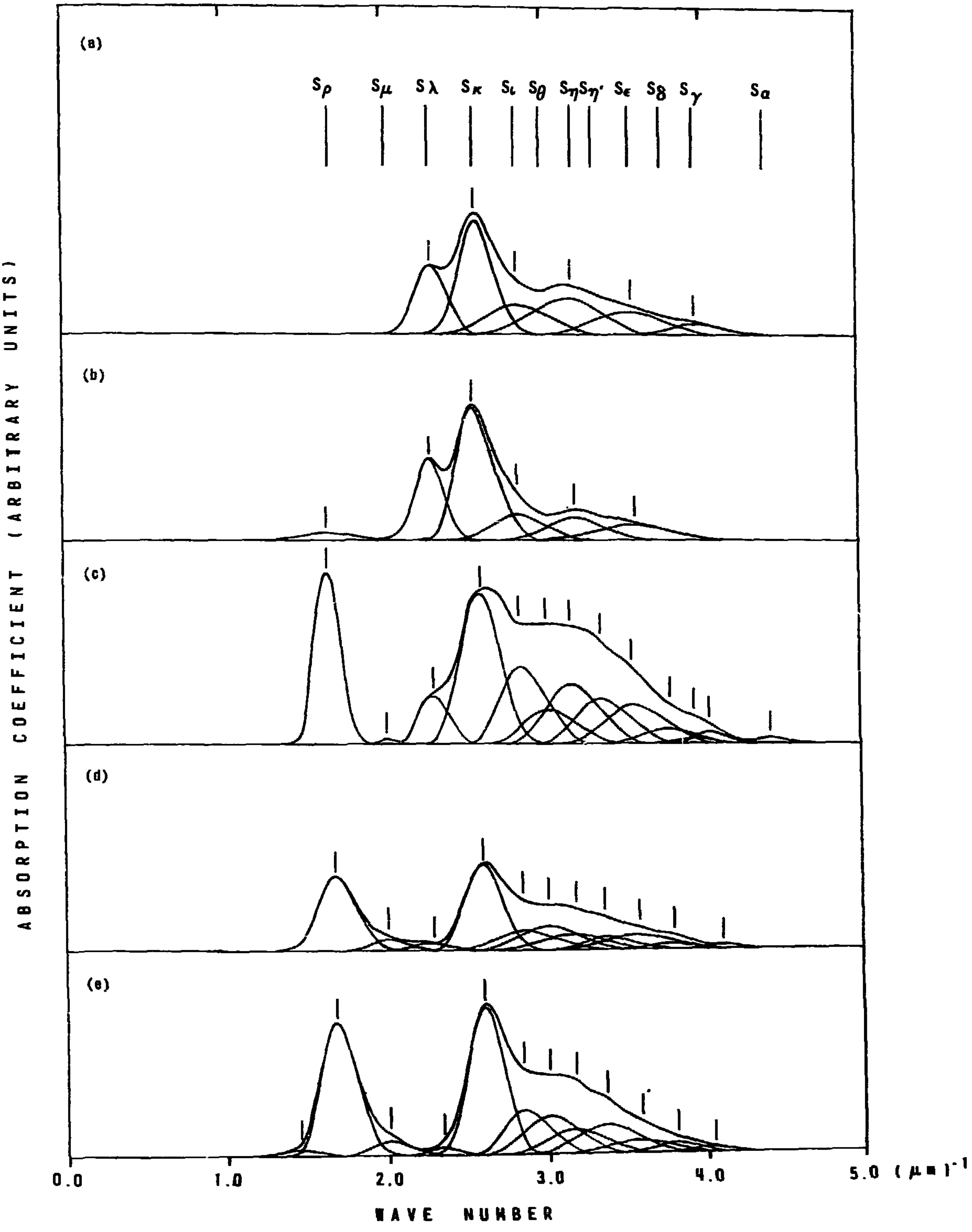


FIGURE 2 ABSORPTION SPECTRA FOR Na-DOPED CaF_2
ANNEALED AT (a) 200°C (b) 135°C

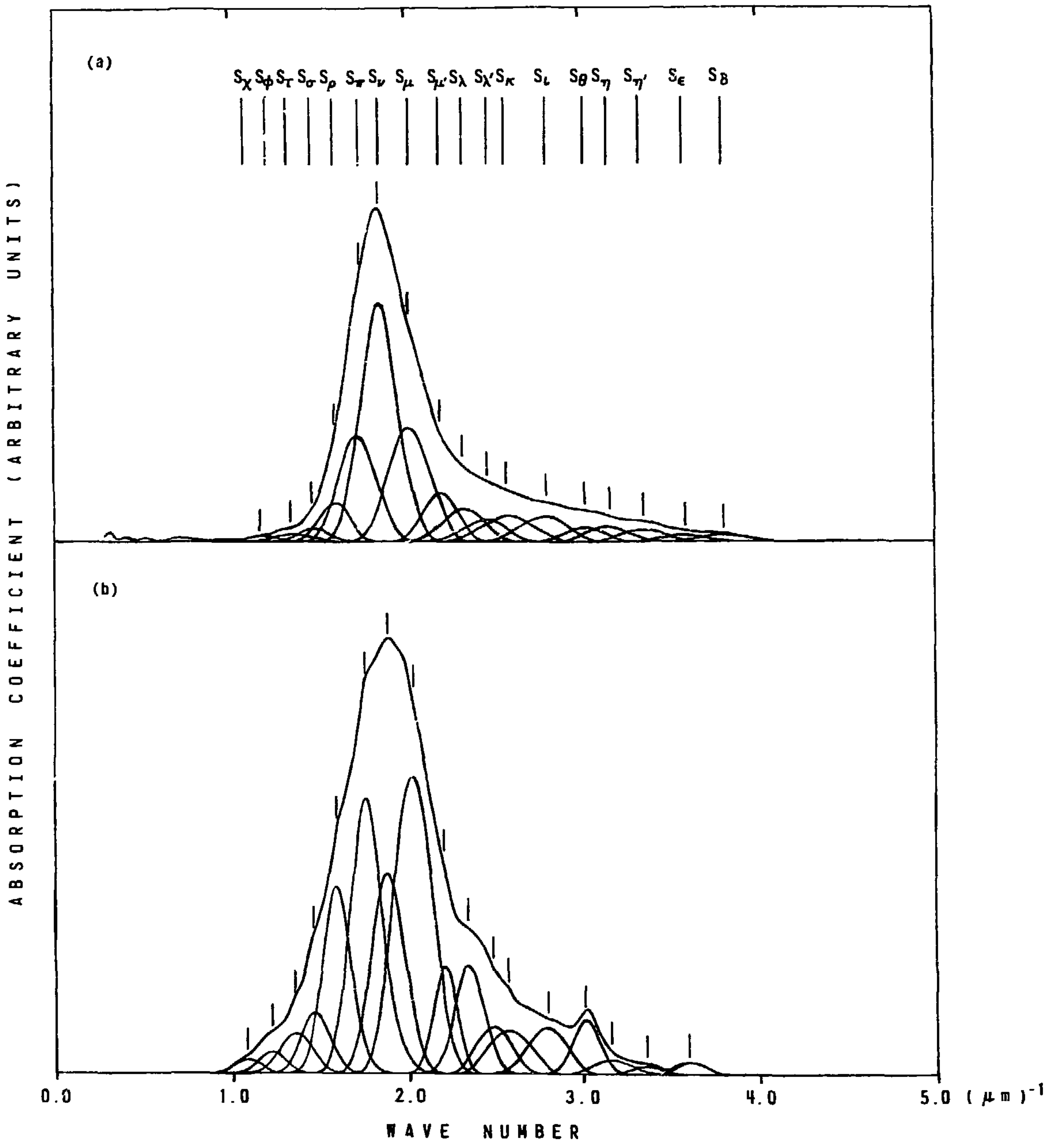


FIGURE 3 ANNEALING BEHAVIOR OF ABSORPTION BANDS FOR CaF_2:NaF (SCHEMATIC)

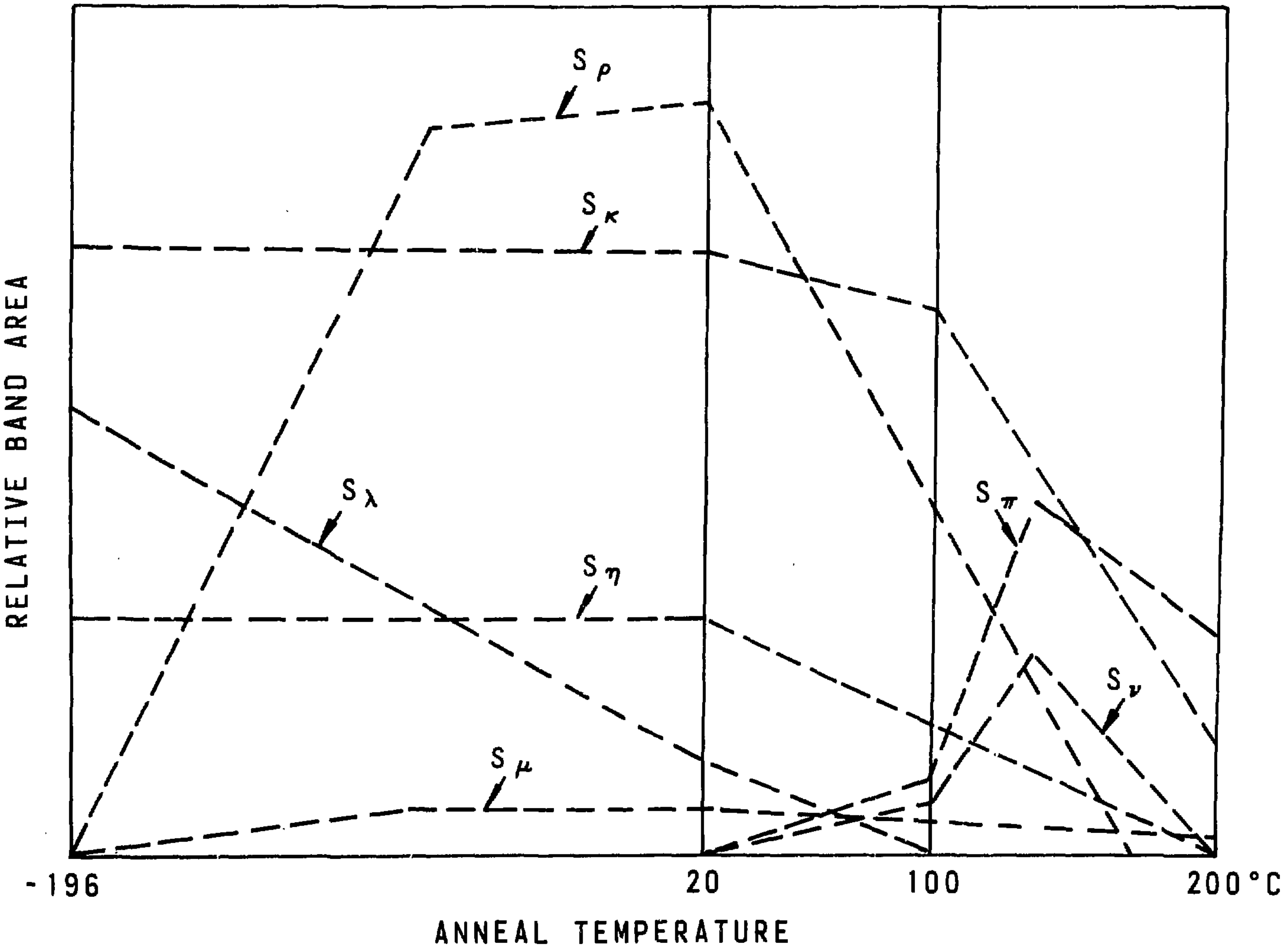


FIGURE 4 ABSORPTION SPECTRA FOR Y-DOPED CaF_2

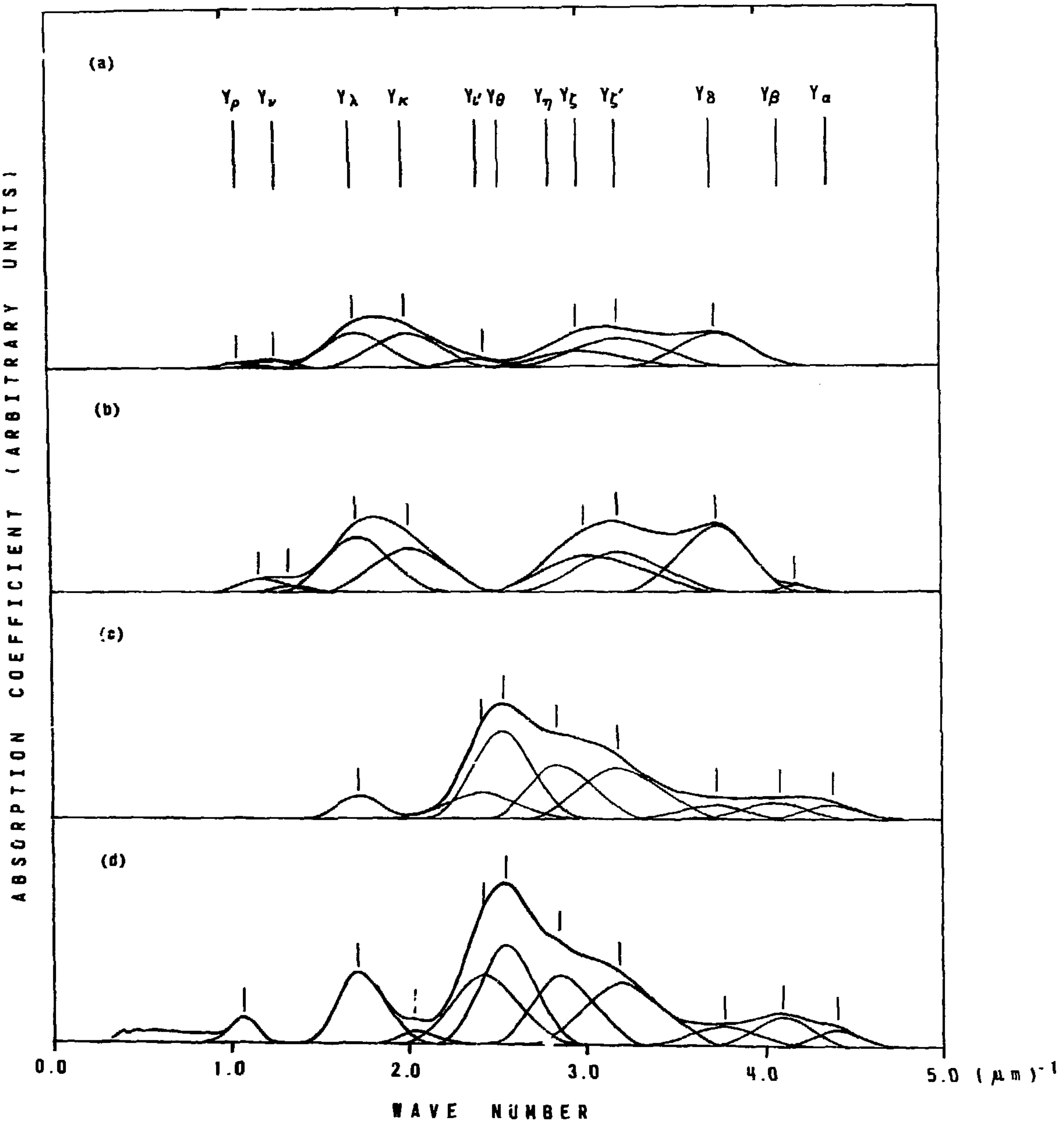
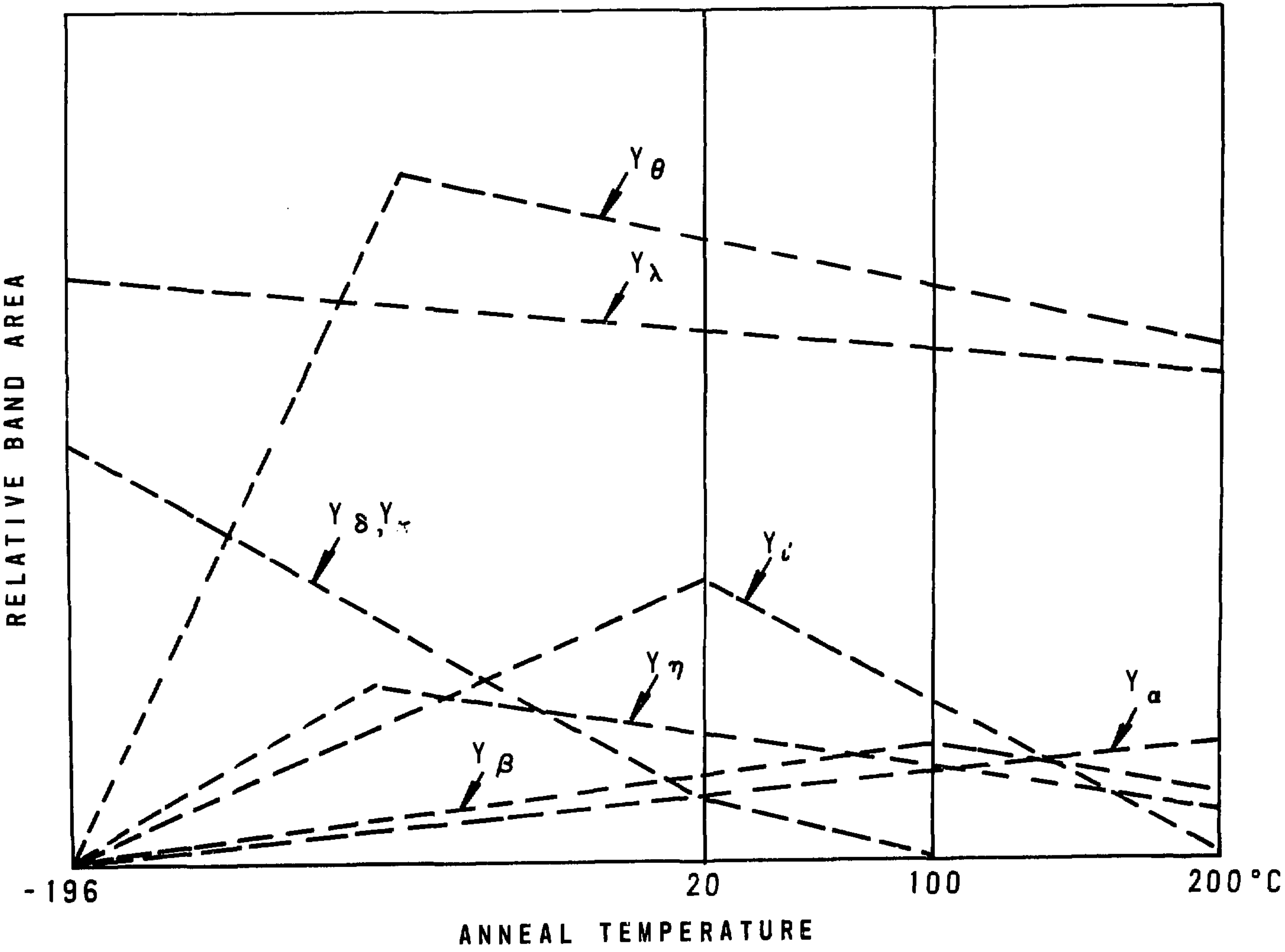


FIGURE 5 ANNEALING BEHAVIOR OF ABSORPTION BANDS FOR CaF_2: YF_3 (SCHEMATIC)



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