

## Depth profiles of interstitial halogen defects in high-energy ion-bombarded RbI by micro-Raman spectroscopy

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Micro-Raman spectroscopy has been used to measure the depth profiles of halogen aggregates in both x-irradiated and ion-bombarded RbI. In experiments using argon ions of energy 13.6 MeV/A, it is shown that the  $I_n^-$  clusters are significantly enhanced in the region of large excitation density near the maximum in electronic energy loss at the expense of the  $I_3^-$  defects. The investigations of fluence dependence show that the number of  $I_3^-$  defects is progressively enhanced with increasing fluence at all depths within the damaged region. The results are examined in the light of current theoretical models of ion-beam interactions with alkali halides.

The extensive literature on the characteristic optical spectra of irradiation-induced defects in alkali halides has proved advantageous in studies of ion-beam interactions with these prototype ionic compounds.<sup>1,2</sup> The conventional techniques of optical absorption and luminescence have provided only average behavior by integrating the variations of specific defect concentrations along the ion tracks. Only rarely, as in the work of Perez and co-workers using very high-energy ions,<sup>3,4</sup> have the defect concentration profiles along the tracks been established by optical absorption using special microspectrophotometric methods. These studies were restricted to  $F$  and  $F_2$  centers and showed substantial agreement with the form of the electronic energy-loss profiles including the maximum near the end of the ion range and were interpreted using a model<sup>5</sup> in which the electronic stopping is dominant. Here the energy is considered to be localized in tracks containing the  $\delta$  rays<sup>6</sup> emitted along the ion trajectories which in turn create the primary defects. The analysis showed no obvious evidence for a different mechanism of defect creation and thus it may be concluded that the normal excitonic mechanism<sup>7,8</sup> is operative. Each track was considered to be saturated with isolated  $F$  centers (based on experiments with  $\gamma$  irradiations of comparable dose) and to have an increasing radius with decreasing ion energy along the ion path. The efficiency of  $F_2$  center formation obeyed a power-law relation with that of  $F$  centers. Track overlap effects are shown to lead to a relative enhancement of  $F$ -aggregate center production. Indeed, at sufficiently high fluences, the depth profiles for isolated  $F$  centers become relatively flat; this suggests that the degree of track overlap initially present in

the region of the maximum of the electronic stopping and where the track radii are largest now extends to the regions closer to the crystal surface. At this stage the separated tracks will have largely disappeared and the damaged volume is essentially homogeneous in the sense of being fully saturated with isolated  $F$  centers.

In the present studies, we have exploited the recently improved understanding of radiation damage processes in alkali halides achieved by a significant number of Raman light-scattering experiments. These indicate the structure of the halogen interstitial defects<sup>9</sup> and their aggregates<sup>10-16</sup> by means of their characteristic dynamical modes. The theory of such Raman scattering by defects is given by Zhou, Goovaerts, and Schoemaker.<sup>17</sup> In RbI, the subject of the present work, the dominant iodine aggregates formed during irradiations at ambient temperature have been shown to be of the form  $I_3^-$  and  $I_n^-$  ( $n=5,7,\dots$ ).<sup>11,16</sup> We have now made micro-Raman measurements of their respective concentration profiles along the ion tracks in ion-bombarded RbI. It was previously appreciated that under the prevailing conditions of high excitation density, halogen aggregation processes are enhanced;<sup>18</sup> the presently developed techniques clearly show the interrelationship between the aggregates at the various positions along the ion tracks and thus provide information on their formation. Similar methods could be used for other materials amenable to optical studies.

Ion bombardments with  ${}_{36}\text{Ar}^{17+}$  ions of energy 13.6 MeV/A were performed on RbI crystals maintained at 300 K, while for comparison purposes a similar crystal was x irradiated at 300 K using a tungsten-target tube operated at

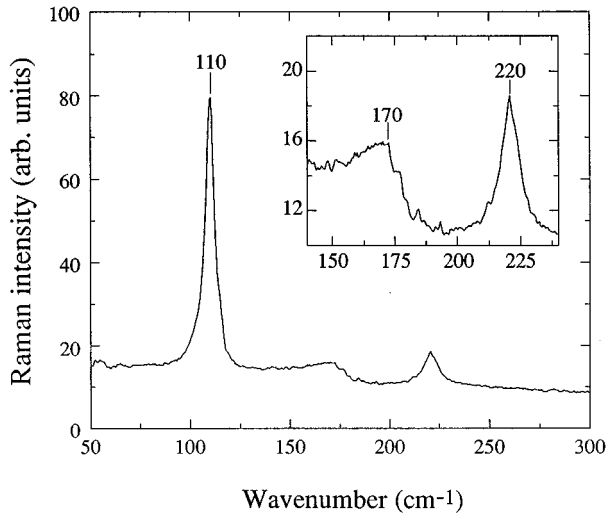


FIG. 1. Raman spectrum of RbI bombarded at room temperature with argon ions at a fluence of  $2 \times 10^{13}$  ions/cm<sup>2</sup>. The spectrum was measured near the surface of the sample in a backscattering geometry at 80 K using laser illumination of wavelength 514.5 nm.

50 kV and 20 mA. In order to prevent optical bleaching of the color centers, the crystals were maintained at 80 K by means of a low-temperature stage used with the Raman microscope. The spectrometer was arranged in the triple subtractive configuration and a cooled CCD detector provided the necessary sensitivity and low noise performance. Micro-Raman measurements were made at closely spaced positions perpendicular to the direction of the ion or x-ray beam to yield the defect concentration profiles. In addition, a conventional Raman measurement was made on the front surface of an ion-bombarded specimen using a backscattering configuration. Polarization measurements were not attempted as previous experience<sup>19</sup> has shown that reorientation of the  $I_3^-$  ions can occur under illumination thus preventing the application of the powerful behavior-type method of determining defect symmetries.<sup>17</sup>

The results of the conventional Raman backscattering measurement are shown in Fig. 1 and are in accord with previous Raman spectra obtained from x- and  $\gamma$ -irradiated RbI in respect to the spectral features present.<sup>11,16</sup> A dominant feature is the 110 cm<sup>-1</sup> peak due to  $I_3^-$  ions with its overtone at 221 cm<sup>-1</sup>. In addition, a broader and weaker band in the region of 170 cm<sup>-1</sup> is observed arising from the presence of  $I_n^-$  ( $n = 5, 7, \dots$ ) aggregates. Experimental studies to date have suggested that these higher-order polyiodides are created from the  $I_3^-$  ions in the process of halogen aggregation.<sup>12</sup> Thus a variation in the relative concentration of these species would be expected according to the local electronic excitation density as discussed earlier.

The general form of the spectra obtained with the Raman microscope is very similar to that shown in Fig. 1. As an illustration, the spectra measured at three different depths from the surface on which the argon ions were incident are shown in Fig. 2 for a fluence of  $2 \times 10^{13}$  ions/cm<sup>2</sup>. It is noted that whereas the 110 cm<sup>-1</sup> peak and its first overtone at 221 cm<sup>-1</sup> associated with the  $I_3^-$  ions decrease with increasing depth, the 171 cm<sup>-1</sup> band from the  $I_n^-$  aggregates increases.

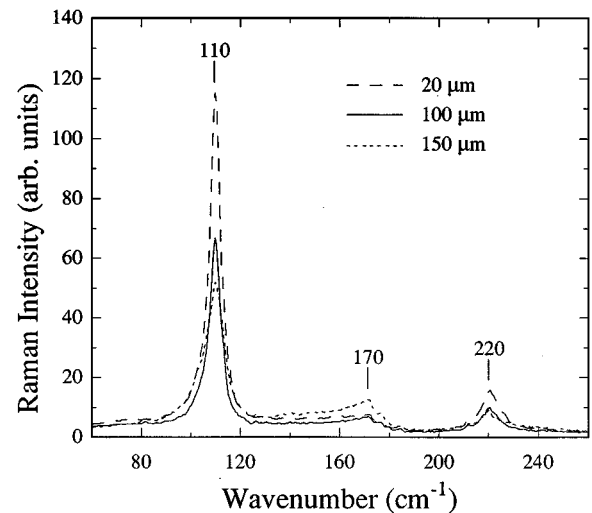


FIG. 2. Spectra measured with the Raman microscope at three different depths from the surface on which the 13.6 MeV/A argon ions were incident. The fluence was  $2.0 \times 10^{13}$  ions/cm<sup>2</sup>. The dashed line is for a depth of 20  $\mu\text{m}$ , the solid line for 100  $\mu\text{m}$ , and the dotted line for 150  $\mu\text{m}$ .

In Fig. 3, we show the depth profiles of the numbers of  $I_3^-$  and  $I_n^-$  aggregates for argon-ion bombardment at three different fluences ranging from  $0.5 \times 10^{13}$  to  $2 \times 10^{13}$  ions/cm<sup>2</sup>. In these measurements the relative concentrations of the respective defects were determined from the peak intensities of their Raman bands above background. Owing to the asymmetric shape and broad, weak nature of the 170 cm<sup>-1</sup> band this was considered a more reliable procedure than attempting a detailed line-shape analysis. The most obvious feature is the peak in the number of  $I_n^-$  aggregates in fair agreement with the maximum in the electronic energy loss as determined by a TRIM-92 simulation.<sup>20</sup> It should be appreciated that with these high ion energies, there is a sensitivity of the ion range to the stopping powers used; indeed alternative calculations vary by up to 10%.<sup>21</sup> The influence of nuclear stopping was also evaluated in the same TRIM calculation. This is a very small contributor to the total stopping power even in the region of the peak in nuclear stopping. The latter is very sharp, being within the final 3  $\mu\text{m}$  of the ion range, and does not agree with the form or the position of the maximum in the  $I_n^-$ -aggregate concentration. Possible defect creation by direct displacements cannot be ruled out, but, in present, must be of minor importance in the present context. The position of the maximum in the number of  $I_n^-$  aggregates varies in a consistent manner, occurring at progressively larger depth values with increasing fluence. Associated with the development of this maximum is a reduction in the numbers of  $I_3^-$  centers (relative to the energy deposition represented in the TRIM calculation), indicating that the two effects are coupled and providing particularly clear evidence that the higher-order polyiodides are part of a continuous process of halogen aggregation. The overall number of  $I_3^-$  defects increases with increasing fluence. The large degree of ion track overlap leading to the fully saturated conditions throughout the damaged volume in respect to isolated  $F$  centers in experiments on LiF at comparable fluence levels,<sup>4</sup>

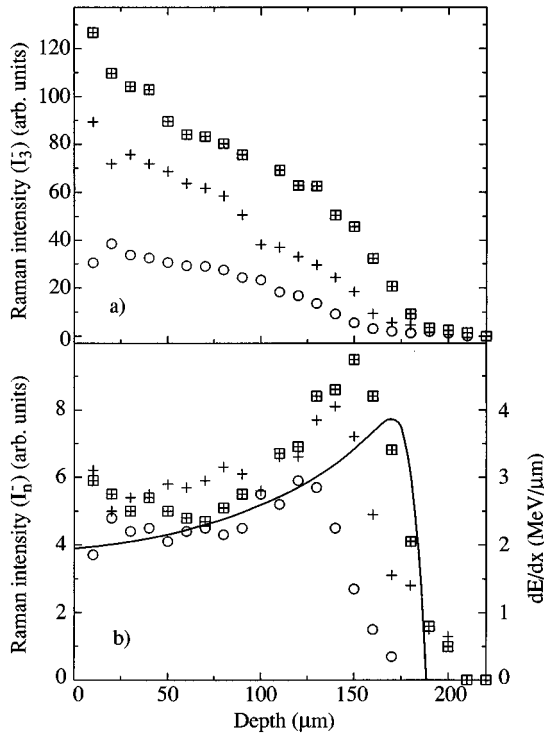


FIG. 3. (a) Depth profiles of  $I_3^-$  clusters at various fluences for RbI bombarded with 13.6 MeV/A argon ions at 300 K: open circles: for a fluence of  $0.5 \times 10^{13}$  ions/cm<sup>2</sup>; crosses: for a fluence of  $1.0 \times 10^{13}$  ions/cm<sup>2</sup>; squares: for a fluence of  $2.0 \times 10^{13}$  ions/cm<sup>2</sup>. Micro-Raman measurements were conducted at 80 K using laser excitation of wavelength 514.5 nm. (b) Corresponding depth profiles for  $I_n^-$  aggregates at the same fluences as in (a). The same symbols are used for the corresponding fluence values. The solid curve shows the electronic energy deposition profile (Ref. 20) calculated using TRIM-92.

apparently have not been attained in the present experiments on RbI in regard to the smallest halogen aggregates; a tendency towards saturation throughout the whole volume would favor the higher-order aggregates at the expense of the smaller clusters.

In Fig. 4, the concentration profiles for  $I_3^-$  and  $I_n^-$  defects are shown for the x-rayed specimen. Again from the respective Raman peak intensities the  $I_3^-$  species are dominant. Both defects show a monotonic decrease in concentration in accord with calculations of the x-ray energy deposition with depth, taking into account the variations of x-ray-absorption coefficient with the spectrum of x-ray energies;<sup>22</sup> the results again follow the predictions of the excitonic mechanism and represent profiles using Raman spectroscopy. They are clearly different in form from those in the case of ion bombardment.

The results indicate that halogen aggregation in the form of polyiodides is promoted in regions of especially high electronic excitation energy density. The precise relationship between the  $I_3^-$  and  $I_n^-$  clusters at a particular depth will depend on several factors. In the case of ion bombardment where saturation within the ion tracks or throughout the crystal volume has not been reached for these defects, then their respective numbers will depend critically on their mutually

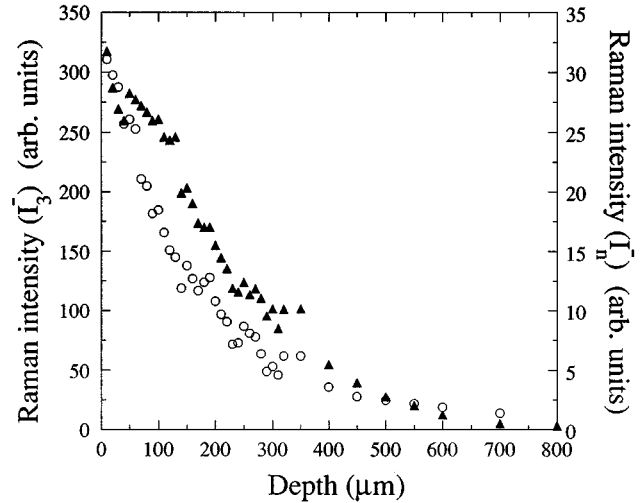


FIG. 4. Depth profiles of  $I_3^-$  (open circles) and  $I_n^-$  (closed triangles) halogen clusters of RbI x irradiated at 300 K. Micro-Raman measurements were conducted at 80 K using laser excitation of wavelength 514.5 nm.

coupled growth kinetics and their dose and dose-rate dependence, as well as the degree of ion track overlap. This latter factor could be significant at the fluences used particularly in the regions near the end of the ion range where the radii of the tracks becomes progressively larger as the ion energy decreases according to the model of Perez, Balanzat, and Duval.<sup>4</sup> A further effect which emerged from previous studies of RbI by  $\gamma$  irradiation at 300 K is that a significant part of the complete inventory of halogen clusters appears Raman inactive.<sup>16</sup> Further aggregation of this type, as well as defect proximity and diffusion effects in cluster formation at the end of the ion range are expected to influence the precise form of the peak in the number of  $I_n^-$  aggregates and their relationship to the electronic energy-loss profile. A more detailed discussion of these effects in experiments on a variety of alkali halides will appear in a more comprehensive paper.<sup>23</sup> The results for the x-rayed crystal show the potential of the approach in a situation which is inherently simpler than that for ion bombardment. As mentioned above the relative concentrations of the respective halogen clusters will depend on dose and dose rate and on the details of the growth kinetics. A study of the evolution of the depth profiles with a range of x doses would be of considerable value in this regard.

The results give a clear indication of the depth profiles and provide new information on the defects measured; they show the potential of micro-Raman spectroscopy in general for ion-beam profiling in which variables such as temperature can be varied. They also provide new insights into halogen interstitial aggregation and the kinetics of their growth under conditions of low- and high-energy deposition rates for the respective cases of x rays and high-energy ions. The information provided is complementary to the studies on ion-bombarded LiF by Perez, Balanzat, and Duval<sup>4</sup> discussed earlier.

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