Radiation-induced Compaction in the laboratory-made soda-lime glass caused by 100 MeV Ag+7 ions

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Abstract

The radiation-induced compaction of Soda Lime glass at various ion flounces is discussed in this paper. Radiation-induced compaction is investigated by measuring intrinsic qualities like density and refractive index. The absorption band in optical properties and FTIR spectroscopy analysis are also used to investigate radiation-induced compaction. Radiation-induced absorption bands in the visible range are produced by the E'center and non-bridging oxygen hole centres, according to an experimental study. Before and after irradiation, the Urbach energy and bandgap energy were calculated. Radiation-induced structural modification and changes in glass composition have been attributed to the decrease in energy gap values. The radiolysis of Si–O–Si bonds have been used to explain changes in the FTIR spectrum caused by ion irradiation.
Keywords: E' center, non-bridging oxygen hole centers, Urbach energy

1. Introduction

Radiation-induced defects are caused by major changes in material characteristics such as chemical, electrical, magnetic, mechanical, optical, and so on, as a result of high-energy radiation [1] Ionization and displacement effects are the two types of radiation effects that could be identified. In a good conductor, the ionization effects will fade quickly and will just contribute to the material's heating. In an insulator, however, the electrons released by ionization may be retained at various lattice defects, resulting in more or less permanent changes in the material. When glasses are irradiated with ionizing radiation, such as x-rays, γ-rays, or ultraviolet light, they undergo significant changes in optical and structural properties[2]. They show strong optical absorption bands in the visible and ultraviolet ranges. The non-bridging oxygen hole centers, E' centers are the most fundamental radiation-induced defects (or color centers) in silicate glasses.

The high-energy swift heavy ion (SHI) collides with atoms in the material and loses energy through electronic and nuclear processes known as electronic energy loss (Se) and nuclear energy loss (Sn). When an ion is passed through a glass material, point defects, defects clusters, and ion tracks can develop along with the ion projected range and at the end of the trajectory[3]. The electronic energy loss (dE/dX)e and nuclear energy loss (dE/dX)n of 100MeV Ag ion along the projected range using TRIM calculations. In case of soda-lime glass , electronic energy loss $(dE/dX)_e = 7.17X10^{19}$ eV/μm and nuclear energy loss $(dE/dX)_n = 3.029X\ 10^{16}$ eV/ μm of 100MeV Ag ion along the projected range is estimated as 16.50 μm and the stopping power is 27 MeV cm^2/gm .

In the case of ion irradiation, the contribution of electronic energy loss (S_e) is much more than that of nuclear energy loss. It has been suggested that the defects formation in Soda Lime glass under high energy heavy ions irradiation is highly related to the electronic energy losses

The fundamental radiation-induced defects (or color centres) in silicate glasses are (i) The nonbridging oxygen hole centres (NBOHCs) (NBOHC:≡ Si–O∗) occur at 4.8eV, (ii)The E' centre (≡Si∗)is observed at 5.8 eV, (iii) The oxygen deficiency centre (ODC ≡Si-Si≡) at 5.0 eV and (iv) The peroxy radical (POR:≡ Si–O–O∗) at 2.0 eV, where the notation ≡ represents three bonds with other oxygens in the

glass network and ∗ denotes an unpaired electron[4]. A defect like the H_2^+ centre is observed due to the impurity introduced in the manufacturing process. The absorption band at 444nm is attributed to H_2^+ centre[5]

2. Experimental Details

A. Sample Preparation

In the laboratory, a Soda Lime glass is fabricated with the following composition: 60 SiO_2 + 22 Na_2O + 12 K_2O + 2MgO + 2CaO + 2 TiO_2

In this case, SiO_2 is used as a Glass Former, (Na_2O + K_2O) is used as a Network Modifier (MgO + CaO) used as a Stabiliser, and TiO_2 is used as an R.I. improver

The batch calculations for the above glass are shown in the table

Name of compound	Formula	% by weight	Batch calculations (gms)
Silica	SiO_2	60%	12
Sodium carbonate	Na_2CO_3	22%	8.0511
Potassium carbonate	K_2CO_3	12%	2.2598
Magnesium carbonate	$MgCO_3$	2%	0.5136
Calcium carbonate	$CaCO_3$	2%	0.6145
Titanium dioxide	TiO_2	2%	0.4

Table-1 Batch calculations of compositions (in grams) for the soda-lime glass

The combination is melted at 1250°C, then removed and annealed in a mold for two hours at 600°C. The sheet is polished and sliced into 1cm X 1cm X 0.1cm samples. To eliminate any surface ambiguity, the samples were cleaned in acetone, distilled water, and then methyl alcohol. These samples were then dried and covered in aluminum paper before being kept in a dust-free area.

B.Irradiation

These samples were then dried and covered in aluminum paper before being kept in a dust-free area. The samples were subsequently irradiated with 100 MeV Ag7+ ions from the 15 UD pelletron accelerator at Interuniversity Accelerator Center, New Delhi, India. The fluence was varied from sample to sample in the range of 1×10^{12} *ions/cm*^{2} *to* 5×10^{13} *ions/cm*^{2}. The irradiation was carried out in a high vacuum (» 10^{-8} torr) and at room temperature.

C. Density Measurements

Mettler Toledo density measurement kit, also known as Gravimetric, Buoyancy kit, is used to determine the density of irradiated glass samples and control samples. The sample is weighed in air and then again in a known-density auxiliary liquid. The measurement is accurate to within ±0.1 percent. The density is measured for a virgin sample and five different ion flounces. The given result is based on the average of at least five measurements for each ion fluence.

D. Measurement of Refractive Index

The Refractive index is a function of the composition and thermal history of the glass. Several methods for measuring refractive index, along with their advantages and limitations and the procedure for laboratory annealing, Here Becke line method is a method for determining the refractive index of a 100MeV Ag+7 irradiated glasses relative to its surrounding medium. The Becke line will always move toward the higher refractive index medium when the distance is increased and will move toward the lower refractive index medium when the distance is decreased from the point of critical focus. Using this method, the refractive index of irradiated glass can be determined with an accuracy of ± 0.001. e. A wavelength filter is used to produce monochromatic light, the experiment is carried out at 589nm for the Becke line method.

E. UV-Visible Spectroscopy

UV-Visible Spectroscopy is measured using a JASCO V-750 UV-Visible Spectrophotometer with double-beam, single monochromator, variable spectral bandwidth, and a photomultiplier tube (PMT) detector. The experiment spans the wavelength range of 200 nm to 800 nm, and the instrument's accuracy is +/-0.2 nm (at 656.1 nm).

F. Bandwidth measurement

The plot of $(\alpha h\upsilon)^{1/2}$ against $h\upsilon$ is used to calculate the optical band gap (α is called the absorption coefficient, $h\upsilon$ is the energy of the incident photon) and is determined by the extrapolation of the linear portion of this graph to $(\alpha h\upsilon)^{1/2} = 0$[6].

G. Urbach energy Calculations

Urbach law $\alpha h\upsilon = \alpha_0 \exp(h\upsilon/E_0)$ is used to calculate Urbach energy E_0 (α_0 is constant). The graph of α against $h\upsilon$ is fitted to $y = a \exp(bx)$ and the Urbach energy $E_0 = 1/b$ is calculated. The changes in the parameter of the optical bandgap and the Urbach energy are indicative of the change in the structure of the soda-lime glass[7].

H. FTIR Spectroscopy

FTIR spectroscopy is carried out by JASCO-FTIR-4000 FTIR Spectrometer. The wavelength range is wavenumber range 7800 to 350 cm^{-1} and non-hygroscopic KRS-5 windows and a Peltier stabilized DLaTGS detector With a resolution of 0.7cm^{-1}.

3. Result and Discussion

A. Analysis of Density variation:

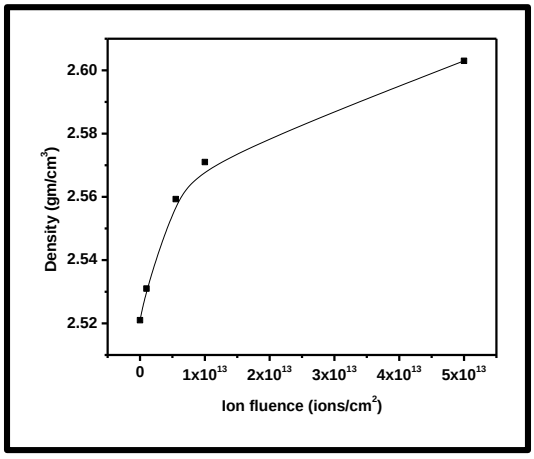


Figure 1. The density of Soda Lime glasses as a function of ion fluence

The effect of ion fluence on the density of Soda Lime glasses is shown in Fig. 1. It is seen that with an increase in ion fluence, the density of soda-lime glass increases. The trend is not linear. The increase in the density is 8.22%. This phenomenon is called compaction because the process involves an increase in density. The glass structure has an equilibrium after the softening temperature. After the glass is subjected to irradiation of 100Mev Ag +7, the structure or constitution of the glass would rearrange itself rapidly after the irradiation [8]. The study was carried out with respect to time. After 30 days the same observations were carried out. There is no change in the density with time. This indicates that the structure of the constituent after the irradiation is permanently changed. This indicates that compaction is more fluence sensitive not time-sensitive.

B. Analysis of Refractive Index:

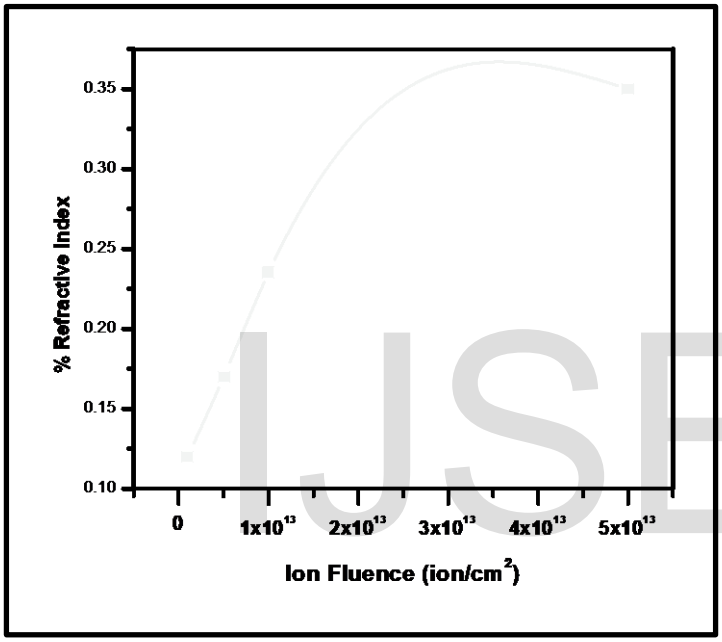


Figure 2. The % Refractive Index of Soda Lime glass with ion fluence

The calcium to barium ratio in the glass has a significant influence on its refractive index due to the presence of Ca_2^+ and Ba_2^+ cations in the glass structure. Na ions are weakly bound in a structure due to the presence of Ca^+ and Ba^+ ions. When the quantity of Ba_2^+ ions increases, they may create ionic bridge links with two oxygen ions linked to SiO_4 tetrahedra. The volume contraction or compacting effect of ions might be responsible for the rise in refractive index. The average coordination number of oxygen is reduced because of other oxides. This is the cause of the change in the refractive index[9].

The significant rise in the refractive index of glass samples exposed to $5X10^{13}$ ions/cm^2can be explained in the following way. The difference between unirradiated and irradiated silicate glass is not in the length of the Si—O bond, which is the same in both cases, but in the reduced Si-Si distance, which indicates a smaller Si-O—Si bond angle. The rise in the refractive index is also attributed to distortion in the Si-O-Si structure caused by a change in the bond angle. Furthermore, the formation of oxygen hole centers irradiation can reasonably be taken to mean rupture of covalent bonds gives rise to change in the refractive index [10],[11].

C. UV-VIS spectral analysis

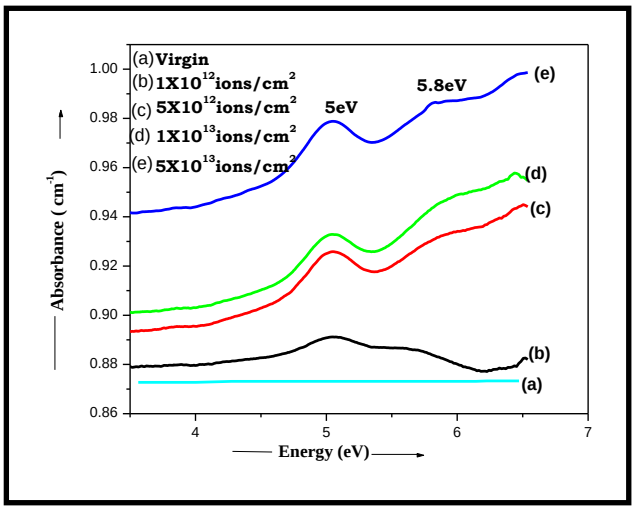


Figure 3. The UV visible absorption spectra of virgin and ion irradiated Soda Lime glass

The UV Visible absorption spectra of Soda Lime glass before and after ion irradiation are shown in the figure. Ion irradiated Soda Lime glass has one distinctive absorption band with maxima at 476 nm, but virgin Soda Lime glass does not reveal any. It's also worth noting that increasing ion fluence has little influence on the position of the band which remains constant, although increasing ion fluence increases the intensity of the peaks. The increase in the intensity of the peak with an increase in the ion fluence suggests that only the concentration of the defects is increased by the ion fluence. The peak at 5eV belongs to ODC, whereas the peak at 5.8eV relates to E'.

The fundamental defects created intrinsically from Si—0—Si

A paramagnetic boron center can in principle originate from three different radiation-induced mechanisms:

$$\text{Si-O-Si} + h\nu \longrightarrow \text{NBOHC} + E' \qquad (1)$$

$$2E' + h\nu \longleftrightarrow \text{ODC} \qquad (2)$$

Reaction (1) is photo induced network breakage and creation of NBOHC and E' absorption centres and in reaction (2) E' centres can form ODC centres or vice versa In those cases the defects are formed by breaking a Si-O or a Si-O bond, and the diamagnetic precursor is then converted into E' center. [12,13]

D. Analysis of Bandgap

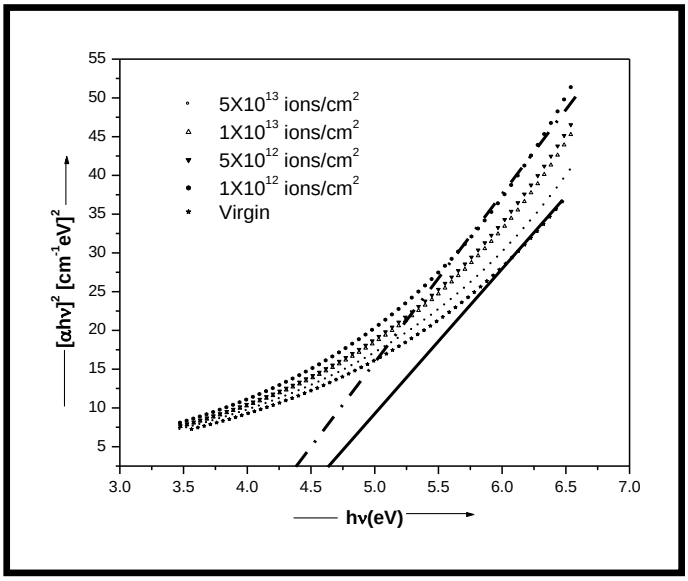


Figure 4. The plot of $(\alpha h\upsilon)^{1/2}$ against

The absorption coefficient (α) was expressed in the quadratic form in the high absorption region.

UV Visible spectroscopy can be used to determine an absorption coefficient. It varies concerning hv. It is given by tau'c equation

$$\alpha(h\upsilon) = \left[\frac{(h\upsilon - E_{opt)}}{h\upsilon}^2\right]$$

The plot of $[\alpha(h\upsilon)]^2$ versus hv is plotted to determine the energy bandgap. After extrapolating the tangent to the curve on the x-axis, the energy band gap is computed. is observed that, with increased ion fluence, the magnitude of the bandgap energy seems to decrease. It is shown in figure-4.

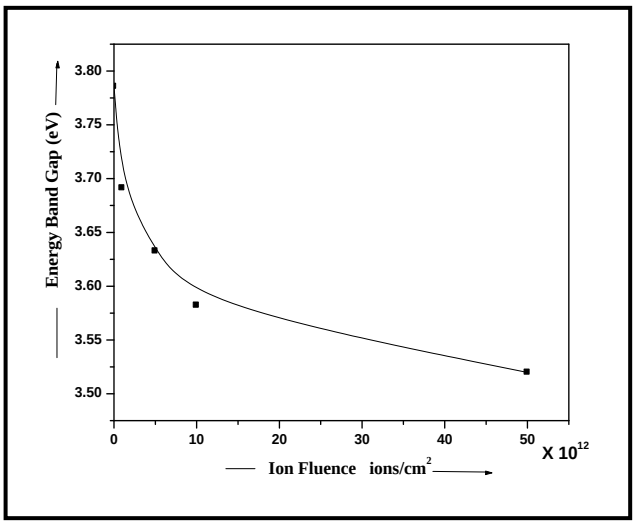


Figure 4. The UV visible absorption spectra of virgin and ion irradiated Soda Lime glass

E.Urbach energy Analysis

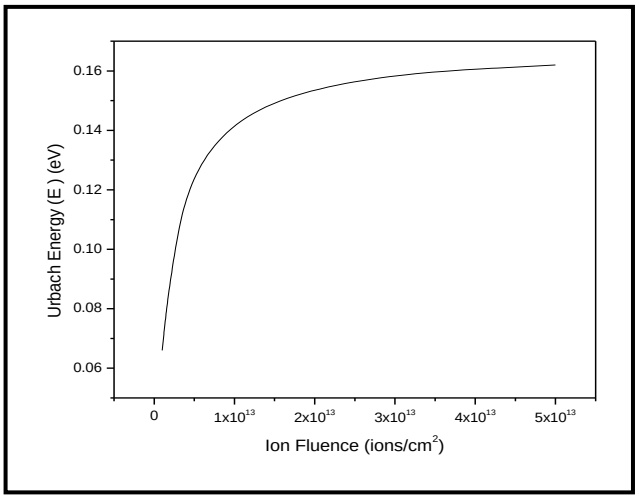
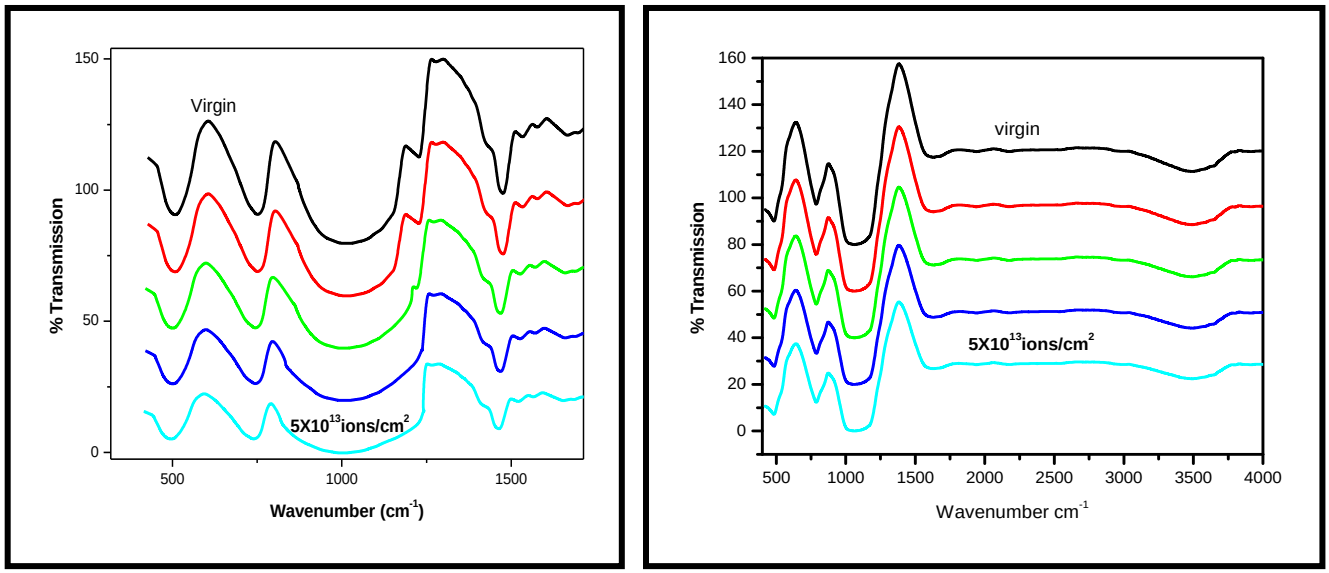


Figure 5. Urbach energy as a function of ion fluence

Urbach energy is usually ascribed to the measure of the structural disorder. The formation of a localised state with energies at the boundaries of the energy gap is one of the effects of the structural disorder on the electronic structure of amorphous materials. The calculated values of Urbach energies are plotted with the different ion fluence which is shown in Figure Urbach energy increases with an increase in the ion fluence. This clearly shows that the degree of structural disorder causing damage to the glass structure has increased significantly[14]. A structural disorder induced by ion fluence is one of the causes of glass compaction[15].



(a) **(b)**

Figure 6. (a) FTIR Spectra of virgin and ion irradiated Soda Lime glass at different ion fluences (appended) in the range 400 - 1500 cm^{-1} (b) FTIR spectra 500- 4000 cm^{-1}

F. FTIR spectral analysis

The figure shows the Fourier transform infrared spectra (FTIR) of Soda Lime glass irradiated with 100 MeV Ag^{7+}ion. All the spectral curves reveal the fundamental IR bands characteristic of the structural silicate chains. The observed bands can be attributed to the specific groups or the cation vibrations The principal FTIR frequencies are classified into three regions

(a) The mid-region extending from 16000 to 4000 cm^{-1} is characterized by the appearance of the characteristic absorption bands of the network forming group or silicate group.
(b) The near-infrared region extending from 4000 to 400 cm^{-1} comprises absorption bands due to vibrations of water, hydroxyl, and sinol SiOH groups.
(c) The far-infrared region after 400 cm^{-1} is characterized by the presence of sharp narrow consecutive peaks belonging to the vibrations of network modifier cations.

The main absorption bands of the Soda Lime glass are located at 503, 750, 1019,1224, and 1472 cm^{-1} with some other minor peaks at 1200-1500cm^{-1} .

(1) Strong transmission band at 504 cm^{-1} is observed, which is attributed to Si–O–Si or O–Si–O bending modes
(2) Small absorption band at 750 cm^{-1}, is assigned to Si–O–Si symmetric stretching of bridging oxygen between tetrahedral or Si-O-Si symmetric stretching of bridging oxygen
(4) Strong broad absorption band at 1019 cm^{-1} is the Symmetric stretching vibration of (ionic group) which can be impurities in the glass
(5) The peak at 1235 cm-1 is not assigned to any band.

(5) Very weak inflection at 1472 cm^{-1}, which is the overtone Si-O-Si symmetric stretching of bridging oxygen.
(6) The band centered at 3675cm^{-1} is the confirmation of H_2^+ centre is assigned to a hydroxyl group (SiOH) [16,17,18]

The transmission intensity of all the bands decreases with increasing ion fluence while some bands become broader without any change in the band peak position.
The decrease in the band intensity and its broadening is due to the Si-O-Si bond scission with ion irradiation.
Moreover, the broadening of the shoulder is a manifestation of a statistical distribution of different bonding arrangements at each silicon atom site. The shift of the peak position is an indicator of a change in the average bond angle and the shift towards a smaller wavenumber corresponds to the smaller bond angle.

The angle in silica glass for the Si–O–Si bond is spread between 120° and 180°, and it is highly unstable at smaller values. When Soda Lime glass is irradiated by ions, the momentum, and energy of the impacting particle are transmitted directly to atoms in the glass network or crystal lattice. The atoms (Si, O) that have been impacted will be shifted into interstitial locations. There is also a phase shift in which the structure has the lowest free energy. It differs from the unirradiated phase by lowering the most likely Si-O-Si angle by about 10°. This phenomenon is called radiation-induced compaction.

The Si–O–Si bond scission following successive ion irradiation results in a decrease in band intensity and broadening, followed by a shift in bond angles, which indicates structural compaction[19,20]

4. Conclusions

Radiation-induced compaction of Soda Lime glass of various ion fluences is studied utilizing density and refractive index as a function of ion fluence. This is due to a structural change in the glass, as confirmed by UV-VIS and FTIR measurements. The defects are caused by the origin of the E' centres, NBOHC and ODC are due to the scission of the Si-O-Si bond induced by ion irradiation. Urbach energy and band gap calculations are used to support the phenomena of compaction as a result of structural change.

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