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Equilibrium and nonequilibrium distribution of aliovalent light-impurity ions in simple oxides

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The effects of atmosphere and cooling rate from elevated temperatures on the distribution of Li impurities in MgO, and Mg impurities in Al_2O_3 crystals are reported. At sufficiently high temperatures, regardless of the atmosphere, Li^+ ions from Li_2O precipitates in MgO, and Mg^{2+} ions from $MgAl_2O_4$ precipitates in Al_2O_3 are dispersed around the precipitates, forming complex-oxide regions rich in these impurities, referred to as microgalaxies. Fast cooling of these crystals freezes the nonequilibrium distribution of these impurities surrounding the precipitates. However, if the crystals are cooled sufficiently slowly, the system has ample time to establish an equilibrium distribution, with most of the Li and Mg ions returning to the Li_2O and $MgAl_2O_4$ precipitates respectively. Based on the microgalaxy model, it is not unrealistic to expect that oxygen vacancies would be formed within the microgalaxy, regardless of the atmosphere.

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I. INTRODUCTION

Simple oxides such as MgO and Al_2O_3 have a strong tendency to remain stoichiometric. To create nonstoichiometric oxygen vacancies in these two simple oxides requires extremely stringent conditions: ≈7 atm of Mg vapor up to 2200 K for[1,2] MgO and ≈2300 K for Al_2O_3 crystals in Al vapor.[3] In the present study, we demonstrate that in Li-doped MgO and in Mg-doped Al_2O_3, nonstoichiometric oxygen vacancies can be formed at much lower temperatures.

There are several similarities between MgO:Li and Al_2O_3:Mg crystals: in both systems the doped light impurities are present in three forms: (a) In MgO there are randomly distributed Li^+ ions substituting for Mg^{2+} ions, just as there are randomly distributed Mg^{2+} ions substituting for Al^{3+} ions in Al_2O_3.[4–6] The net charge surrounding the aliovalent impurities is therefore negative, such that a hole can be trapped during ionizing radiation. In MgO:Li, $[Li]^0$ centers (substitutional Li^+ ion with a trapped hole hopping among the six nearest neighboring (NN) oxygen sites) are formed. In Al_2O_3:Mg, $[Mg]^0$ centers (substitutional Mg^{2+} ions with a trapped hole shared by the six NN oxygen ions) are likewise formed. These trapped-hole centers are generally stable only at low temperatures.[7–9] (b) There are Li_2O precipitates[10] in MgO, just as there are $MgAl_2O_4$ precipitates[11–13] in Al_2O_3. These second phases have been identified by transmission electron microscopy (TEM). (c) There are regions of high concentration of substitutional Li^+ ions, surrounding the Li_2O precipitates in MgO,[4–7] just as there are regions of high concentration of Mg^{2+} ions surrounding the $MgAl_2O_4$ precipitates. These Li-solute clouds surrounding the precipitates have been referred to as "microgalaxies." It was first observed that upon *oxidation* at high temperatures, highly stable $[Li]^0$ centers in MgO were formed.[4–7] TEM demonstrated that the Li_2O precipitates were much smaller in oxidized crystals.[10] Subsequently, highly stable $[Mg]^0$ centers were also observed in Al_2O_3[11,14–18] The thermally generated stable $[Li]^0$ centers in MgO and $[Mg]^0$ centers in Al_2O_3 were spectroscopically identical to the unstable species generated by ionizing radiation. The high stability is due to high concentrations of the trapped-hole centers so that charge neutrality within the *microgalaxy* requires that the aliovalent impurity ions are predominantly in the neutral charge $[Li]^0$ and $[Mg]^0$ states.[4,6] Leakage of a few holes from these impurities will result in a corresponding negative charge in the microgalaxy, thereby preventing further leakage and result in stable $[Li]^0$ and $[Mg]^0$ centers.[16,17,19,20] In the case of MgO, the $[Li]^0$ center is responsible for the conversion of this wide band-gap insulator into a *p*-type semiconductor with an acceptor level 0.7 eV above the valence band.[19,20]

In the present work, the influence of atmosphere (oxygen vs reducing) and cooling rate (slow vs fast) on the thermal generation of defects in MgO:Li and Al_2O_3:Mg crystals was investigated by optical absorption measurements. An extension of the microgalaxy model is made for MgO:Li and Al_2O_3:Mg crystals subjected to thermochemical *reduction* (TCR) at high temperatures. TCR disperses Li^+ and Mg^{2+} ions from the Li_2O and $MgAl_2O_4$ precipitates, respectively, giving rise to localized environments surrounding the precipitates (microgalaxies) which are Li^+ rich in MgO and Mg^{2+} rich in Al_2O_3. We shall reason that oxygen deficiency prevails in both cases. Results in hydrogen-doped MgO crystals will also be discussed to support our reasoning regarding the diffusion of light impurities to form precipitates.

When as-grown MgO:Li and Al_2O_3:Mg crystals are heated and fast cooled, regardless of the atmosphere, the resulting microgalaxies can be regarded as complex-oxide domains in a sea of simple oxides: $Mg_{(1-x)}Li_xO$ in MgO and $Al_{(2-y)}Mg_yO_3$ in Al_2O_3. These complex oxides are responsible for fascinating properties, such as *p*-type semiconducting[19,20] and rapid proton diffusion[21,22] in MgO:Li. The present investigation demonstrates that nonstoichiometric oxygen vacancies can be introduced into Al_2O_3:Mg at much lower temperatures than in the Al_2O_3 simple oxide. The study of cooling rates, or the equilibrium and nonequilibrium distribution of Li and Mg ions in these oxides, provides an insight into the physics of the transition from simple to complex oxides in the same oxide.

II. EXPERIMENTAL PROCEDURES

Single crystals of MgO used in this study were grown at the Oak Ridge National Laboratory by an arc-fusion technique using high-purity MgO powder from the Kanto Chemical Company, Japan.[23] Lithium doping was achieved by mixing 5% of Li_2CO_3 powder with MgO powder before crystal growth. The concentration of lithium impurities in the resulting crystals was approximately 0.04 at. % (400 ppm). MgO crystals intentionally doped with hydrogen were produced by presoaking the starting MgO powder with water. The resulting crystals were very cloudy due to the presence of cavities containing high-pressure hydrogen gas.[22,24,25] Samples with [100] faces and thickness of about 1 mm were obtained by cleaving and were chemically polished in hot phosphoric acid.

The α-Al_2O_3:Mg single crystals were grown by the Czochralski method at BICRON Crystal Products. Atomic emission spectrometry analysis indicated that the magnesium concentration was $\approx$25 ppm. Samples of about 1 mm thick were cut from the boule with the *c* axis perpendicular to the broad face, and polished to optical transparency.

Optical absorption measurements in the UV-VIS-IR regions were made with a Perkin-Elmer Lambda 19 spectrophotometer. Mid-infrared data were taken with a Perkin-Elmer FT-IR 2000 spectrophotometer. In luminescence experiments the samples were excited with a low-intensity UV light, the source being a 400-W HgXe lamp in conjunction with a 7200 Oriel monochromator set at 250 nm. The emitted light was focused into the entrance slit of a SPEX 1000M monochromator and detected with a Hamamatsu R943-02 cooled photomultiplier. The spectra were recorded with a SR400 gated photon counter. For low temperature measurements, the samples were placed inside a Leybold closed-cycle-helium cryostat.

Oxidizing treatments were made in flowing oxygen gas (99.9% pure) with the samples placed in a platinum basket inside an alumina tube inserted in the horizontal, axial hole of a CHESA furnace. TCR was performed with the samples placed inside an enclosed graphite chamber inserted in the alumina tube with flowing nitrogen gas (99.9% pure). Samples were heated at the desired temperature for 15 min and fast cooled, dropping into a liquid nitrogen bath, or slow cooled to room temperature (RT) at a rate of 1 K/min.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The influence of fast cooling versus slow cooling on the thermal generation of defects was investigated by heating MgO:Li, MgO:H, and Al_2O_3:Mg in either an oxidizing or reducing atmosphere.

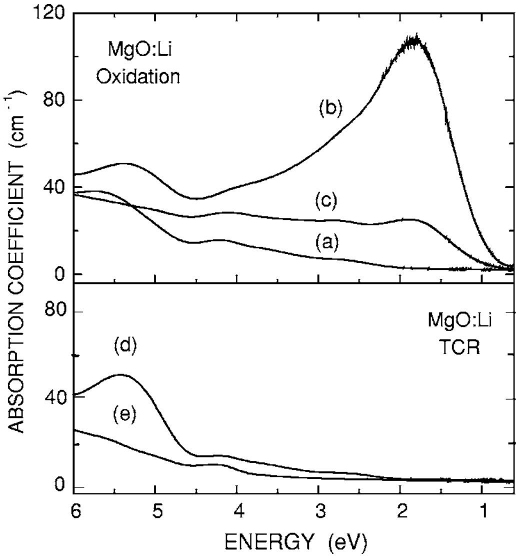

FIG. 1. Optical absorption spectra of an MgO:Li sample: (a) as-grown, (b) oxidized at 1600 K, followed by fast cooling, (c) oxidized at 1600 K, followed by slow cooling, (d) TCR at 1600 K, followed by fast cooling, and (e) TCR at 1600 K, followed by slow cooling. The thickness of the sample was 0.7 mm.

A. Lithium-doped MgO crystals

An as-grown MgO:Li sample was heated at $T=1600$ K in flowing oxygen, followed by fast cooling into liquid nitrogen. The optical absorption spectra in the UV-VIS-IR and in the mid infrared regions were measured at RT. Subsequently, the same sample was oxidized again at $T=1600$ K and slow cooled to RT.

Figure 1 shows the UV-VIS-IR spectra before (trace *a*) and after the oxidizing treatments. A broad and intense optical absorption band at 1.83 eV was apparent after oxidation followed by fast cooling (trace *b*). This band has been identified as due to the stable $[Li]^0$ centers.[5,7] At sufficiently high temperatures, Li^+ ions from Li_2O precipitates dispersed and occupied Mg^{2+} sites surrounding the precipitates, giving rise to a localized lithium-rich environment. In effect, two Li^+ ions and one O^{2-} ion from the Li_2O diffuse out, resulting in oxygen-deficient microgalaxies.[5] The neighboring Mg^{2+} ions are replaced by the Li^+ ions. The resulting lack of positive charges relative to the lattice is compensated by positive holes provided by the molecular oxygen adsorbed from the atmosphere, when the oxygen molecule becomes ionic

$$O_2 \rightarrow 2O^{2-} + 4 \text{ holes}.$$

These free holes are trapped by the charge imbalance surrounding the precipitates

$$Li_2O + \frac{1}{2}O_2 \rightarrow 2(Li^+O^-),$$

where (Li^+O^-) is the $[Li]^0$ center with a hole trapped at a neighboring O^{2-} ion.

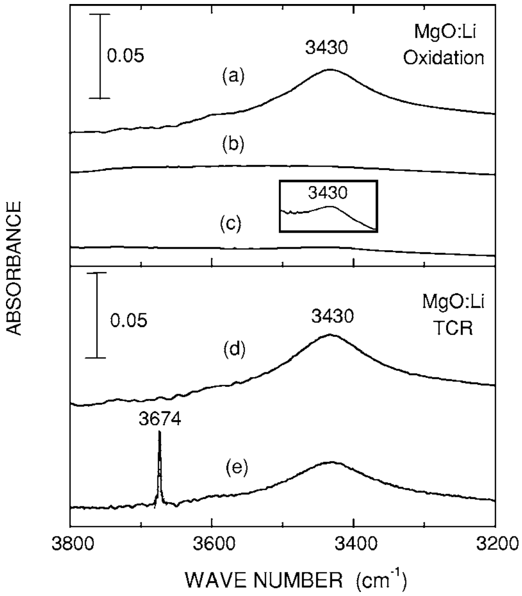

FIG. 2. absorption spectra of an MgO:Li sample: (a) as-grown, (b) oxidized at 1600 K, followed by fast cooling, (c) oxidized at 1600 K, followed by slow cooling; in the inset the band at 3430 cm^{-1} is magnified 20× in the vertical direction, (d) TCR at 1600 K, followed by fast cooling, and (e) TCR at 1600 K, followed by slow cooling. The thickness of the sample was 0.7 mm.

In addition, a less intense band at 5.3 eV is observed, which has been previously attributed to a nonparamagnetic oxygen-vacancy complex involving lithium ions.[27] Subsequent oxidation, followed by slow cooling, decreased the $[\mathrm{Li}]^0$ concentration by ≈80%, and the absorption at 5.3 eV completely vanished (trace *c*). These results indicate that under equilibrium, Li^+ ions in the microgalaxy had returned to the precipitates.

MgO:Li crystals have a strong affinity for hydrogen. While it is possible to grow MgO crystals with virtually undetectable concentration of protons, it has not been possible to grow MgO:Li without a large amount of hydrogen.[21,22,28,29] In the as-grown state, MgO:Li crystals exhibit a very broad IR band at 3430 cm^{-1} associated[21,22,28,29] with OH^- complexes perturbed by Li^+ ions (trace *a* in Fig. 2). The sharp absorptions at 3296 cm^{-1} and 3700 cm^{-1}, which are the most common OH^- stretching frequencies observed in lithium-free crystals,[22,30,31] were absent. These two absorptions are due to V_{OH}^- centers (H^+ substituting for a Mg^{2+} ion and thus negatively charged relative to the lattice) and $\mathrm{Mg(OH)_2}$ precipitates, respectively.[22,30,31] While there is an abundance of hydrogen in the crystal, no $\mathrm{Mg(OH)_2}$ precipitates have been observed in MgO:Li, regardless of heat treatments. After oxidation at 1600 K followed by fast cooling, the 3430 cm^{-1} band was undetectable, suggesting that most of the hydrogen diffused out of the crystal (trace *b*) The protons are highly mobile at 1600 K. It has been shown that there is a deuteron-proton exchange in MgO:Li crystals even at 773 K in $\mathrm{D_2O}$vapor.[21] A small amount of hydrogen is restored by reoxidizing and slow cooling the sample [see Fig. 2(c) and inset].

TCR of the same sample resulted in the disappearance of the $[\mathrm{Li}]^0$ band, regardless of whether or not it is followed by fast or slow cooling. The 5.3 eV band re-emerged [Fig. 1(d)] with a larger intensity following fast cooling, and vanished following slow cooling [Fig. 1(e)]. The observation that the latter spectrum resembles that of the as-grown state [Fig. 1(a)] is not surprising because the crystal growth was performed under essentially the same condition: the reduction effect of the graphite arcs, and slow cooling. Under slow cooling, Li^+ ions in the microgalaxy return to the precipitates. The effects of reduction and oxidation are reproducible.

In the OH^--stretching region, reduction at 1600 K followed by fast cooling rejuvenated the initial intensity of the absorption band at 3430 cm^{-1}, indicating that protons were restored in the crystal [Fig. 2(d)]. An important observation is that if the sample was slow-cooled, a sharp band at 3674 cm^{-1} appeared [Fig. 2(e)], with a full width at half maximum (FWHM) of ≈3 cm^{-1}. This band has not been observed before in these crystals and coincides[32] with the hydroxyl stretching frequency in LiOH. The reduction conditions are the same as during crystal growth, and it is not clear why this band was not observed in as-grown crystals.

These results indicate that in MgO:Li at high temperatures, regardless of the atmosphere, Li^+ ions from $\mathrm{Li_2O}$ precipitates form an envelop (microgalaxy) around the precipitates, and consequently, the precipitates diminish in size. The microgalaxy constitutes the basis for the complex oxide, $\mathrm{Mg}_{(1-x)}\mathrm{Li}_x\mathrm{O}$, immersed in a sea of MgO. In an oxidizing atmosphere the adsorbed oxygen serves as the source of holes to form the $[\mathrm{Li}]^0$ centers in the microgalaxy. Subsequent reduction destroys the $[\mathrm{Li}]^0$ centers and restores the protons in the crystal. Fast cooling freezes the nonequilibrium distribution of both lithium and hydrogen impurities. In a reducing atmosphere, there is no source of holes. Even though Li^+ ions form a microgalaxy around a precipitate, there is no source of holes to form $[\mathrm{Li}]^0$ centers. Charge compensation in the microgalaxy requires another mechanism.

B. Hydrogen-doped MgO crystals

The same set of oxidation and reduction experiments was performed in an MgO:H sample at 1600 K. Cooling rates have a stronger effect on the IR spectra than the atmosphere (Fig. 3). The two most prominent IR absorption bands in as-grown MgO:H peak at 3296 and 3700 cm^{-1}, which have been identified as due to V_{OH}^- centers and $\mathrm{Mg(OH)_2}$ precipitates, respectively (Fig. 3).[22,30,31] After fast cooling, the 3296 cm^{-1} band grows at the expense of the 3700 cm^{-1} band, regardless of the atmosphere (traces *a* and *c*). The converse is true for slow cooling (Fig. 3(b) and 3(d)). The relative intensities of the 3296 and 3700 cm^{-1} bands are reversible indefinitely by alternately fast and slow cooling. At sufficiently high temperatures, protons are randomly distributed throughout the crystal and freeze in their substitutional sites during fast cooling, thus forming V_{OH}^- centers. However, if the crystal is slow cooled, the protons will have ample opportunities to aggregate and form $\mathrm{Mg(OH)_2}$ precipitates. These results confirm that whenever MgO:Li and MgO:H systems have enough time to cool, both lithium and hydro-

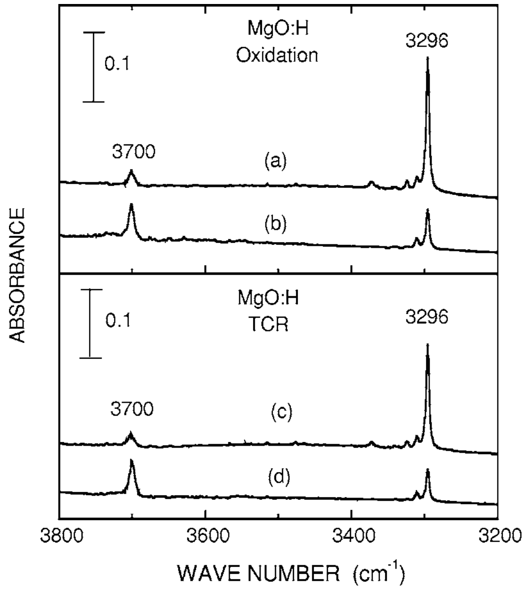

FIG. 3. IR absorption spectra of an MgO:H sample: (a) oxidized at 1600 K, followed by fast cooling, (b) oxidized at 1600 K, followed by slow cooling, (c) TCR at 1600 K, followed by fast cooling, and (e) TCR at 1600 K, followed by slow cooling. The thickness of the sample was 1.1 mm.

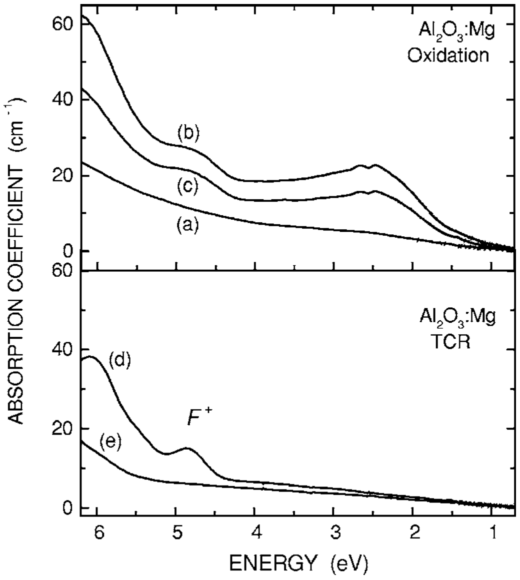

FIG. 4. Unpolarized optical absorption spectra of an Al_2O_3:Mg sample: (a) as-grown, (b) oxidized at 1900 K, followed by fast cooling, (c) oxidized at 1900 K, followed by slow cooling, (d) TCR at 1900 K, followed by fast cooling, and (e) TCR at 1900 K, followed by slow cooling. The thickness of the sample was 1.1 mm. Using polarized light, absorption above 5.5 eV could not be measured.

gen impurities form Li_2O and $Mg(OH)_2$ precipitates, respectively.

C. Magnesium-doped Al_2O_3 crystals

Oxidation: An as-grown α-Al_2O_3:Mg sample (with the *c* axis perpendicular to the broad face) was heated in flowing oxygen at $T=1900$ K and fast cooled in a LN bath. The spectra before and after the oxidation are shown at the top of Fig. 4. In the as-grown state, it exhibits a slight gray-purple coloration due to a broad absorption at $\approx$2.56 eV [Fig. 4(a)]. This band is due to the paramagnetic hole-trapped $[Mg]^0$ center,[11,14] which is the analog of the $[Li]^0$ band in MgO.[7,8] The presence of $[Mg]^0$ centers in as-grown crystals indicates that the crystal-growth condition was slightly oxidizing. (This is not the case in MgO:Li crystals, which were grown under the strongly reducing graphite arcs[22] and consequently $[Li]^0$ centers were not present.) After oxidation followed by fast cooling, the intensity of the 2.56 eV band dramatically increased, yielding[11] a $[Mg]^0$ concentration of about 1×10^{18} cm^{-3} [Fig. 4(b)]. Another band at about 4.75 eV with a FWHM of $\approx$0.5 eV emerged. The defect responsible for this band is uncertain. Subsequent oxidation followed by slow cooling decreased the $[Mg]^0$ concentration by $\approx$35%, while the absorption at 4.75 eV appeared to have decreased slightly [Fig. 4(c)]. These results show that during slow cooling, a significant amount of the dispersed Mg^{2+} ions return to the $MgAl_2O_4$ precipitates.

That the absorption at 4.75 eV is a composite band, with some contribution of the F^+ band (oxygen vacancies with one electron), cannot be ruled out. First, it is sufficiently close to the 4.8 eV peak of the F^+ center.[33–35] Second, the FWHM is roughly the same as or slightly larger than that of the F^+ band. Polarization experiments to determine whether F^+ centers contribute to the 4.75 eV absorption were not conclusive. Luminescence measurements at room temperature and 10 K were also not conclusive due to self-absorption at 3.8 eV where the F^+-center emission occurs.[35]

Reduction: Subsequent thermochemical reduction of the Al_2O_3:Mg sample at 1900 K changes the spectra. After fast cooling, the $[Mg]^0$ band at 2.56 eV completely disappeared [Fig. 4(d)]. In addition, an absorption band at 4.8 eV emerged, which has been identified as due to F^+ centers.[33–35] The resulting concentration[35] of the F^+ centers was $\approx 3 \times 10^{16}$ cm^{-3}. This band vanished following slow cooling after reduction [Fig. 4(e)]. The presence of Mg-dopant facilitates the introduction of anion vacancies and their aggregates. To produce higher concentrations of oxygen vacancies three Al_2O_3:Mg samples were thermochemically reduced for 1 h at three different temperatures: 1923, 1973, and 2033 K, followed by fast cooling. Figure 5 shows the unpolarized absorption spectra after TCR. In all the spectra two bands at 6.0 and 4.8 eV are observed, which have been previously attributed in undopedα-Al_2O_3 crystals to *F* (oxygen vacancies with two electrons) and F^+ centers, respectively.[3,33–37] These bands grow more intense as the temperature of the thermal treatment is raised. At temperatures above 1923 K, a new band centered at 2.87 eV emerges with a FWHM of $\approx$0.3 eV; this is close in position to the 2.75 eV band also observed with a FWHM of $\approx$0.3 eV in undoped neutron-irradiated crystals and previously attributed to dimer (F_2^{2+}) centers.[38] Because individual centers within the microgalaxy are so close together, aggregation of *F*-type centers resulting in higher-order defects is likely to occur.

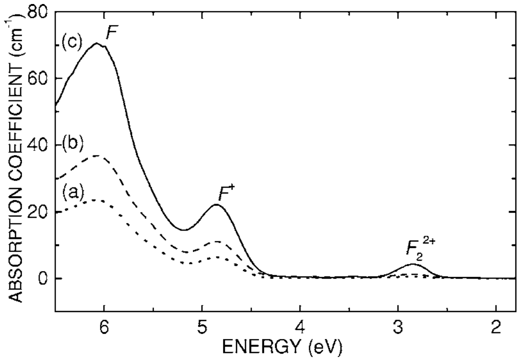

FIG. 5. Unpolarized absorption spectra of Al_2O_3:Mg crystals after TCR for 1 h at 1923, 1973, and 2033 K.

D. Microgalaxy model

The microgalaxy model was first proposed[5,26] to explain the high stability of the thermally generated $[Li]^0$ centers in MgO:Li, as opposed to the unstable centers generated by ionizing radiation. These two types of centers are spectroscopically identical, yet they have vastly different stability. The stable centers are highly concentrated within a domain, called a microgalaxy. While the holes hop from centers to centers within the microgalaxy, they cannot escape the microgalaxy and therefore appear to be thermally stable. It was conjectured that the source of these concentrated $[Li]^0$ centers was the Li_2O precipitates,[5,26] which transmission electron microscopy subsequently confirmed.[10]

This simple model has two implications. The first is that the free hopping of the holes among $[Li]^0$ centers renders the crystal p-type semiconducting.[19,20] While it has not been demonstrated unequivocally that this material is p type, the enhanced electrical conductivity tracks the $[Li]^0$ concentration in the same crystal.[19,20] The acceptor level was estimated to be 0.7 eV above the valence band.[19,20]

The second implication is that oxygen vacancies in both MgO:Li and Al_2O_3:Mg are generated in the microgalaxies, even in oxygen atmosphere. We shall concentrate on the latter. A similar conclusion can be deduced in MgO:Li. In the Al_2O_3 host, the ratio of oxygen ions to cations is 3:2. In the $MgAl_2O_4$ precipitate, it is lower, 4:3. At the temperatures the microgalaxies are formed ($\approx$1900 K), the $MgAl_2O_4$ precipitate is in effect "dissolved" in the Al_2O_3 matrix. Three cations and four oxygen ions dissolved in a matrix of two cations and three oxygen ions result in an excess of cations, or a deficiency of oxygen ions. At this temperature, the adsorbed oxygen from the atmosphere does not in-diffuse rapidly enough to recombine with the oxygen deficiency in the microgalaxy. In TCR crystals, oxygen vacancies in the form of F^+ centers were formed. Without Mg doping, no oxygen vacancies would have been formed in Al_2O_3 under identical conditions. In oxidized crystals, the F^+ centers may well be a component of the 4.75 eV band. Even though we could not demonstrate that the F^+ center was involved, it cannot be ruled out.

Fast-cooling freezes the distribution of the Mg^{2+} ions around the precipitates and forms microgalaxies, regardless of atmosphere. These Mg^{2+} ions would not have time to return to the precipitate. Domains characterized by the complex oxide $Al_{(2-y)}Mg_yO_3$ immersed in the simple oxide Al_2O_3 are expected. If the atmosphere is oxygen, these Mg^{2+} ions will be supplied with holes to form $[Mg]^0$ centers. Hence the $[Mg]^0$ concentration would be highest with fast cooling in an oxygen atmosphere. Slow cooling, on the other hand, gives the substitutional Mg^{2+} ions ample time to return to the precipitates, thereby diminishing the $[Mg]^0$ concentration, even if the atmosphere is oxygen.

In an inert or reducing atmosphere at this temperature, microgalaxies are also formed. There are no holes to supply to the Mg^{2+} ions when Mg^{2+} substitutes for Al^{3+} ions. Therefore $[Mg]^0$ centers would not be observed. The charge compensator is likely to be some form of oxygen vacancies.

IV. SUMMARY AND CONCLUSIONS

The present communication addresses the transport behavior of two types of light-impurity ions within a temperature regime. The first is the super-fast diffuser: protons in MgO. The second category is exemplified by two pseudofast diffusing ions: Li^+ in MgO, and Mg^{2+} in Al_2O_3. The latter category provides unique structure and composition with unusual transport properties. *The microgalaxy can be regarded as a domain of complex oxide in a sea of simple oxide*. It is the microgalaxy that renders unique properties to the host. In the same crystal, actions take place in the complex oxide regime before they occur in the simple oxide.

The influence of atmosphere and cooling rate on the thermal generation of defects was studied in MgO:Li and Al_2O_3:Mg. Because they are partially soluble in the matrix, the dopants form second phases: Li_2O in MgO, and $MgAl_2O_4$ in Al_2O_3. At sufficiently high temperatures, regardless of the atmosphere, the dopants from the precipitates diffuse out and form an envelope (microgalaxies) of substitutional ions. In an oxidizing atmosphere, the substitutional ions are charge compensated by holes forming $[Li]^0$ and $[Mg]^0$ centers, respectively. In MgO:Li, two other effects were observed after the sample was fast cooled: first, an absorption band appears at 5.3 eV, which had previously been associated with a nonparamagnetic defect involving lithium ions and oxygen vacancies;[27] second, the broad OH^--absorption band at 3430 cm^{-1} is absent, indicating that protons diffused out of the crystal. In Al_2O_3:Mg an absorption band at 4.75 eVemerged. The defect responsible for this band has not been identified, although the F^+ center has not been ruled out.

Heating in a reducing atmosphere at 1600 and 1900 K, followed by fast cooling, destroys the $[Li]^0$ and $[Mg]^0$ centers in MgO and Al_2O_3, respectively. In MgO:Li the band at 5.3 eV increased and protons re-emerged. In Al_2O_3:Mg, oxygen vacancies were created. Without the Mg impurities, no anion vacancies would have been formed at 1900 K. In undoped α-Al_2O_3 the temperature needed for the production of F centers by TCR is close to the melting point (2320 K).[3] For example, after 2 h at 2273 K in aluminum vapor, a small concentration of oxygen vacancies was formed: 4×10^{16} cm^{-3} F centers and a negligible amount of F^+ centers.

Thermochemical reduction of Al_2O_3:Mg crystals at temperatures in excess of 1923 K results in clustering of oxygen vacancies to form higher-order defects such as anion-divacancies (F_2^{2+} centers), previously observed only in undoped neutron-irradiated crystals.[38]

Fast cooling freezes the nonequilibrium distribution of both lithium and magnesium ions surrounding the precipitates; however if the crystals are cooled slowly, the system has time to establish an equilibrium distribution with most of the Li and Mg ions returning to the Li_2O and $MgAl_2O_4$ precipitates.

We conclude that microgalaxies formed by these impurities accommodate the formation of defects much more readily than in systems without microgalaxies. The implication is that oxygen vacancies are formed much more readily in complex oxides than in simple oxides, even in an oxygen atmosphere. It is envisioned that complex oxides hold the key to many future discoveries in science and technology. Impurities and defects can be incorporated at much lower temperatures. There are more sites to accommodate both intrinsic and extrinsic defects. As a result, some complex oxides such as magnesium aluminate spinel, $MgAl_2O_4$,[39] and zirconate pyroclore, $Gd_2Zr_2O_7$,[39–41] are more radiation tolerant. The reason why these effects occur is rather simple: the atoms in these oxides are relatively disordered and can easily tolerate displaced atoms caused by radiation.[39–41] An electrical-insulator $12CaO \cdot Al_2O_3$ crystal is converted into an electrical conductor by either incorporation of hydride ions[42] or replacing the interstitial oxygen ions by electrons confined in inert lattice cages.[43,44]

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