Chromium III Centers in Synthetic Alexandrite

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Abstract

The optical absorption of a single crystal of synthetic alexandrite was measured at room temperature using both ordinary and polarized light. Spin-allowed electronic transitions between the $4A_{2g}$ groundstate of the octahedrally coordinated Cr^{3+} ion and a number of quartet states were identified. The broad absorption band due to the first spin-allowed transition ($4A_{2g} \rightarrow 4T_{2g}$) was found to be a complex one which consists of two superimposed bands resultant from absorption by Cr^{3+} ion substituted into two slightly different Al^{3+} sites. Support for two such Cr^{3+} centers—namely, $Cr^{3+}(1)$, and a slightly larger site, $Cr^{3+}(2)$—is provided by their different behavior upon irradiation by X-rays. A possible explanation of the characteristic optical phenomenon (change from green to reddish purple) exhibited by both natural and synthetic alexandrite is discussed. The degree of color change observed in different specimens is attributed to the $Cr^{3+}(1)/Cr^{3+}(2)$ population ratio. The results obtained in the present investigation suggest the possibility of using the $Cr^{3+}(1)/Cr^{3+}(2)$ population ratio—in Cr^{3+}-bearing varieties of alumina minerals—as a geothermometer as well as a geobarometer.

Introduction

Natural alexandrite is a hard, dense, extremely rare, chromium-bearing variety of chrysoberyl ($Al_{(2-x)}Cr_xBeO_4$) which is valued as a gem stone because of its unique and interesting optical properties. Alexandrite is greyish green with a faint reddish tint in daylight and columbine red in incandescent light. Commercially produced synthetic alexandrite crystals exhibit similar optical properties.

Natural alexandrite is isostructural with olivine. Its crystal structure is based on a hexagonal close-packed array of oxygen ions, in which the tetrahedral interstices are occupied by beryllium and the octahedral sites are partially filled by aluminum. X-ray diffraction patterns of the presently investigated synthetic alexandrite single crystals agree with a $BeAl_2O_4$ composition of orthorhombic symmetry. However, a Laue picture suggests that the symmetry might be lower (Arafa, to be published).[1]

Most previous investigators (Farrell and Newnham, 1965; and others) attribute the color of alexandrite to the presence of Cr^{3+} substituting for Al^{3+} in a distorted octahedral site. Some authors cite V^{3+}

as a possible cause of the color. Poole (1964) attributed the color change phenomenon to a "psychophysical" effect on the human eye and brain rather than to any abrupt changes in the properties of the material. White *et al* (1967) favor this view and describe such a color change phenomenon as an "alexandrite effect" in which absorption minima exist at some critical values, relative to the physiological response of the human eye.

Examination of about 15 commercial alexandrite crystals in both daylight and incandescent light revealed variations not only in the degree of the color change from specimen to specimen but also in the reddish tint imparted to the crystals by daylight. The color change was much clearer in specimens having a less reddish tint in daylight. These differences indicate that such change in color, which we agree to call the "alexandrite effect," depends not only on the nature of the incident radiation but also on the concentration and properties of the entities responsible for the color change phenomenon. The present paper is primarily concerned with the behavior of the Cr^{3+} ions in the synthetic alexandrite structure, as related to the observed optical properties. Neutron activation analysis indicated that about 84 ppm of chromium ions are present in the investigated specimen.

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Experimental

Absorption spectra in the 1.0 to 4.5 *eV* region were measured at room temperature versus air, using a Beckman DK–2A Ratio Recording spectrophotometer; no corrections were applied for scattered or reflected light. A polaroid J.-film fitted into a specially constructed holder was used as the polarizer in the 1.0–3.0 *eV* region. The procedure followed in recording the absorption spectra in polarized light was that described by Cohen and Smith (1958). X-irradiation experiments were performed in a General Electric XRD–6 unit operated at 50 kV and 45 mA. The X-ray tube is a water cooled G.E. CA type with a tungsten target. The irradiations were carried out at room temperature at a distance of 5 cm from the source. The specimen was never allowed to stand between runs, in order to minimize the effect of any room temperature thermal bleaching; once the experiment started, data taking continued to completion. Subsequently, the irradiated specimen was heated in air using the same program that was used in all the heating experiments.

Results and Discussions

A single crystal of what is commercially called 'synthetic alexandrite' exhibits a spectrum similar to that of Cr^{3+}-doped alumina (Fig. 1). In the visible region the spectrum consists of 2 major bands at 17,700 cm^{-1} (2.2 *eV*) and 25,800 cm^{-1} (3.2 *eV*), called A and B bands respectively hereafter. Several minor bands are also conspicuous. The A and B bands are assigned the first (ν_1) and second (ν_2) spin-allowed electronic transitions in the partially filled 3*d* shell of the Cr^{3+} ion. Assuming a cubic octahedral field, the Cr^{3+} ion possesses a ^4F ground term which splits under the action of the crystal field to $^4A_{2g}$ (ground), $^4T_{2g}$ and $^4T_{1g}$ states. Another $^4T_{1g}$ state arises from a ^4P term. The complete energy level diagrams, based on quantum mechanical calculations, are given by Tanabe and Sugano (1954). The first spin-allowed transition (ν_1) is just Δ, and we have $D_q = 1770$ cm^{-1} for Cr^{3+} surrounded by 6 oxygens in the present structure. The 3rd spin-allowed transition (ν_3) $^4A_{2g} \rightarrow {}^4T_{1g}$ (*P*) can be calculated using the following formula (Underhill and Billing, 1966)

$$340\, D_q - 18(\nu_2 + \nu_3)D_q + \nu_2\nu_3 = 0 \qquad (1)$$

and should occur at about 40,100 cm^{-1}. Unfortunately, ν_3 does not appear on the spectrum because of a high ultra-violet absorption edge of the host
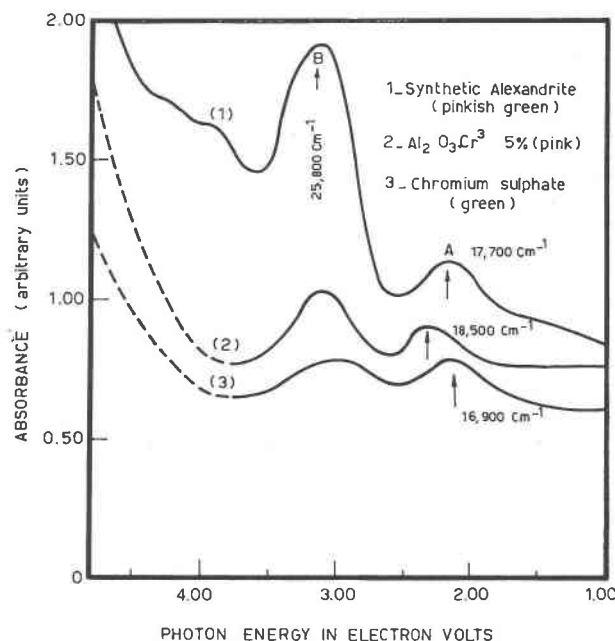

FIG. 1. Absorption spectra of synthetic alexandrite (curve 1), Al_2O_3 doped with 5% Cr^{3+} (curve 2) and chromium sulfate (curve 3).

structure in this same spectral region. Besides, there is always a considerable difficulty in obtaining the true spectrum of such ions as Cr^{3+} in the ultra-violet because this region is generally influenced by traces of Fe^{3+} ion. Neutron activation analysis done for the presently investigated crystal indicated the presence of iron.

As indicated in Table 1, A and B absorption bands observed for synthetic alexandrite occur at frequencies higher than those previously observed and theoretically calculated (Ballhausen, 1962) for the Cr^{3+} ion octahedrally coordinated by oxygen. Since the Cr^{3+} ion ($r = 0.63$Å) occupies in the alexandrite structure a site usually filled by Al^{3+} ions ($r = 0.51$Å), it actually enters a site which is perhaps 16 percent too small. The presence of Cr^{3+} in such a site would cause a kind of compression of the surround-

TABLE 1

Assigned Transitions		Position of Band Maxima (cm⁻¹)		Remarks
Bands	Cr(III)	Experimental Values	Ballhauzen (1962)	
ν_1(A)	$^4A_{2g}$ (F) → $^4T_{2g}$ (F)	17,700	17,400	Spin-Allowed
ν_2(B)	→ $^4T_{1g}$ (F)	25,800	24,500	Spin-Allowed
ν_3	→ $^4T_{1g}$ (P)	Off scale	38,000	Calculated to be about 40,100 cm⁻¹

ing structure and would affect the magnitude of the crystal-field-splitting parameter, Δ. The expression

$$\Delta = Q(r^4)/R^5 \qquad (2)$$

—where Q is the charge on the ligands, r^4 is the mean value of the fourth power of the radii of the d orbital, and R is the metal-ligand interatomic distance—shows that the crystal field splitting is inversely proportional to the fifth power of the interatomic distances. Therefore, the smaller the metal-ligand distance, the greater the value of Δ (Burns, 1969). As a result the absorption bands would be expected to be at slightly shorter wavelengths (as found experimentally) than for Cr^{3+} in a more suitably sized site. In the $BeAl_2O_4$ structure there are several different sites with octahedral symmetry for Cr^{3+} to occupy. Refinement of the structure (Farrell, Fang, and Newnham, 1963) showed that there are two octahedral aluminum sites that differ significantly in size. Half of the aluminum atoms occupy Al(1) sites with inversion symmetry and the remainder are in the Al(2) mirror plane positions. The average nearest neighbor distances are Al(1)–O = 1.890 Å and Al(2)–O = 1.934 Å. Because of the difference in size and symmetry, trivalent cations substituting for Al^{3+} would naturally prefer one site to another. Besides the above mentioned Al-occupied sites, other unoccupied octahedral interstices are also available for the Cr^{3+} ions. The Cr^{3+} ion would preferentially occupy larger sites, denoted $Cr^{3+}(2)$ sites hereafter. However, this does not eliminate the possibility that some Cr^{3+} may occupy the smaller Cr^{3+} (1) sites, especially if introduced into the structure at high temperatures and or pressures. The differences in size and symmetry, *i.e.*, in the crystal field, of the two sites would naturally influence the position and shape of the optical absorption spectrum.

Besides the observed spectral shift, the presence of Cr^{3+} in the smaller site would increase the orbital overlap between $Cr^{3+}(1)$ ion and its ligands. As a result we would expect a gain in the intensity of the absorption bands. This is clearly exhibited by the B band in both synthetic alexandrite and in the Cr^{3+} doped alumina (pink in color), as compared to the green Cr^{3+} compound (Fig. 1). Table 2 shows how the intensity of the B band varies relative to the A band in differently colored Cr^{3+} compounds. Although we do not plan to account for this at present, we feel it is worth mentioning.

The overall absorption spectrum exhibited by the alexandrite crystal (Fig. 1) consists of overlapping

TABLE 2

Substance	Color	I_B/I_A *
Chromium Sulphate	Green	1.00
Chromium Chloride	Bluish green	1.24
Chromium potassium sulphate	Bluish green	1.26
Chromium nitrate	Blue	1.3
$Al_2O_3 \cdot Cr^{3+}$ crystal	Pink	2.2

* The ratio of the intensity of the B band to that of the A band.

absorption spectra of the coexisting $Cr^{3+}(1)$ and $Cr^{3+}(2)$ centers. The breadth of the absorption bands in the A band region favors this view.

Polarized Absorption Spectra of Alexandrite

The absorption spectrum using polarized light showed that the broad absorption in the A band spectral region is not related to a simple band. Figure 2 shows the absorption spectrum of alexandrite if the electric vector ($\mathbf{E}$) of the incident radiation vibrates parallel to the c-axis direction ($\mathbf{E}_{\|c}$, curve 1) and perpendicular to it ($\mathbf{E}_{\perp c}$, curve 2). The absorbance for $\mathbf{E}_{\|c}$ direction, denoted $A_{\|c}$, has a maximum at 17,500 cm^{-1}. For $\mathbf{E}_{\perp c}$, the maximum is at about 18,150 cm^{-1}. The breadth of the $A_{complex}$ absorption band for unpolarized light thus results from superposition of these two slightly different maxima. The $A_{\|c}$ polarized absorption located in the longer wavelength side of the spectrum is attributed to the more populated $Cr^{3+}(2)$ centers and is thought to be responsible for the major greenish color. The $A_{\perp c}$ polarized absorption, located at higher energies, is attributed to the less populated $Cr^{3+}(1)$ centers imparting the faint reddish tint. The compression of the Cr^{3+} ion in the smaller octahedral sites results in a shorter Cr–O distance, and causes the observed spec-
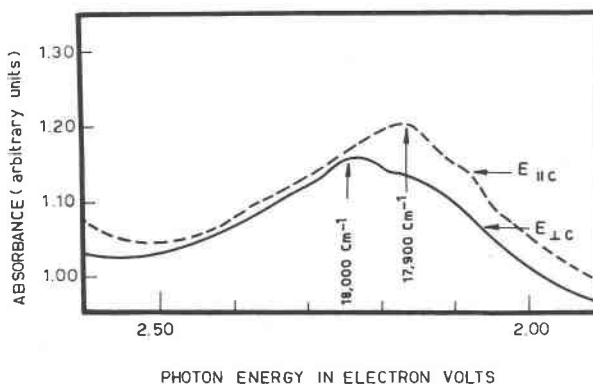

FIG. 2. Polarized absorption spectra of synthetic alexandrite.

tral shift from 17,500 cm^{-1} to 18,150 cm^{-1}. The higher the concentration of the Cr^{3+}(1) centers, the more significant the spectral shift and the clearer the reddish tint. The color imparted by the synthetic alexandrite crystals can be thought of as a function of what we may call the Cr^{3+}(1)/Cr^{3+}(2) population ratio.

Effect of room temperature X-irradiation

Further evidence for the existence of the Cr^{3+} ion in more than one environment is gained from X-irradiation experiments. Small doses of X-irradiation shifted the energy position of the A$_{complex}$ and the B absorption bands towards longer wavelengths (Fig. 3). The observed energy shift in the A$_{complex}$ band and its change in shape perhaps result from a decrease in the intensity of the A$_{\perp c}$ absorption component, attributed to the Cr^{3+}(1) centers, but not of the A$_{\parallel c}$ absorption component. This suggests that only the Cr^{3+}(1) centers responded to the X-ray doses used. It was also noticed that the magnitude of the energy shift at the A$_{complex}$ absorption maximum was not identical with that at the B absorption maximum (Fig. 4). Further irradiation resulted in a sudden and peculiar growth in the B band spectral region (Fig. 5) which appeared unrelated to the growth in the A$_{complex}$ region. The latter continued
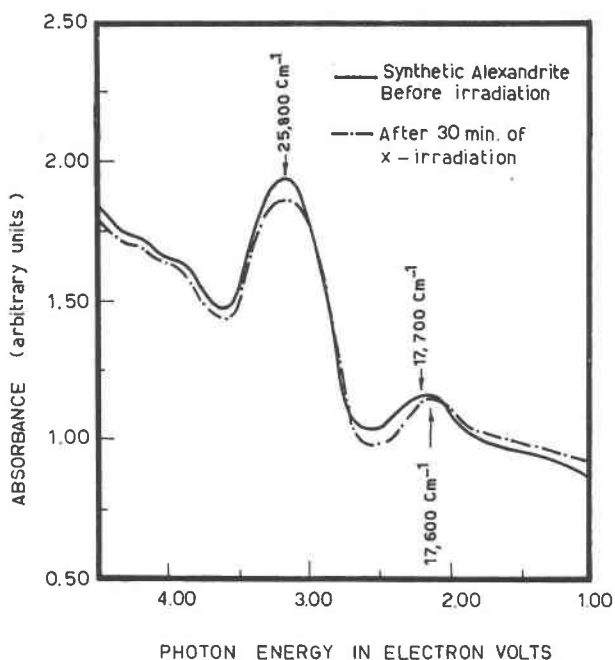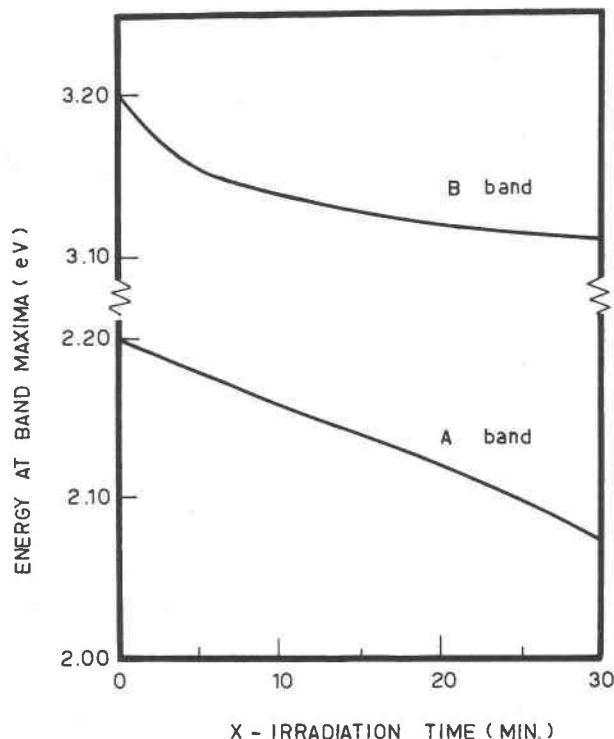

Fig. 4. Change in energy position of the A and B absorption bands in synthetic alexandrite upon X-irradiation (low doses).

Fig. 3. Absorption spectra of synthetic alexandrite before and after 30 minutes of X-irradiation.

to grow at a slow rate. The growth characteristics of both the A$_{complex}$ and the B band upon X-irradiation are shown in Figure 6. The development of a new induced center (X center) in the same spectral region of the B band is quite possible. Hunt and Schuler (1953) observed an absorption band growing upon X-irradiating synthetic corundum (α − Al$_2$O$_3$) at room temperature in the same spectral region. Another small induced absorption band was observed to grow upon X-irradiation in the 14,000 cm^{-1} (1.7 eV) spectral region (Fig. 5). The difference curve shown in Figure 7 clearly illustrates the above observations. Examining transitions in the $3d$ shell of the octahedrally coordinated Cr^{2+} ion shows that the first spin-allowed electronic transition absorbs in the same region. Upon room temperature X-irradiation, the Cr^{3+}(1) may trap electrons and be reduced to Cr^{2+} as follows:

$$Cr^{3+}(1) + e \underset{\text{heat}}{\overset{\text{X-rays}}{\rightleftarrows}} Cr^{2+}(1) \qquad (3)$$
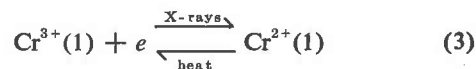
Electron traps other than the Cr^{3+}(1) centers are the Fe^{3+} ions proved to be present in the presently investigated specimen by neutron activation analysis. A
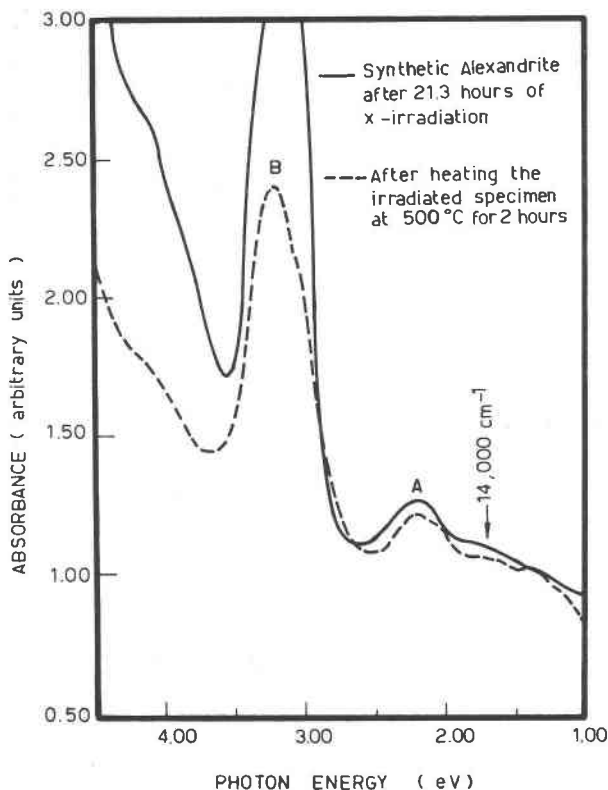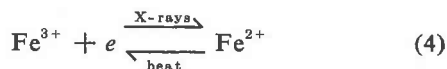
FIG. 5. Optical absorption spectra of synthetic alexandrite before and after 21.3 hours of X-irradiation at room temperature.

FIG. 6. Growth characteristics of the A and B absorption bands in synthetic alexandrite.

slight growth in the near infrared region at about 10,000 cm⁻¹ (1.3 eV), commonly attributed to absorption by Fe^{2+}, also supports the presence of Fe^{3+} and suggests the following radiation-induced reaction:

$$Fe^{3+} + e \xrightleftharpoons[\text{heat}]{\text{X-rays}} Fe^{2+} \qquad (4)$$

The induced center (X center) may tentatively be described as a hole-trap center providing enough electrons to reduce both the Cr^{3+} and the Fe^{3+} ions in the structure. This point needs further investigation. ESR measurements currently being done at Uppsala, Sweden, may reveal the nature of this X-center, (Arafa and others, to be published).

Subsequent to the X-irradiation experiment, the alexandrite specimen was heated in air. The kinetic energy provided by heating the specimen to 500°C was sufficient to return the crystal to its original optical state (Fig. 8).

An observation worth mentioning here is that the specimen exhibited a clear green color while hot (at
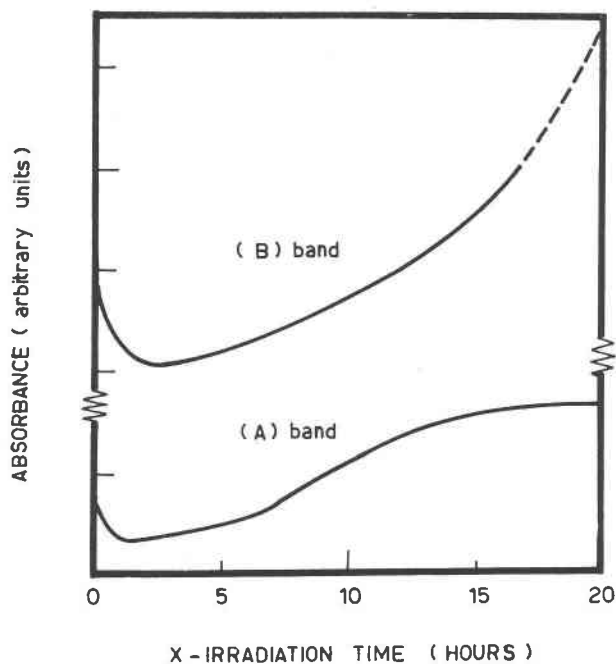
about 600°C). The reddish tint returned gradually upon cooling to room temperature. This may be explained in terms of the lattice expansion which occurs during heating. The smaller sites expand, and the optical shift which is exhibited at room temperature is no longer there. Upon cooling, these sites contract and alter the crystal field splitting parameter and
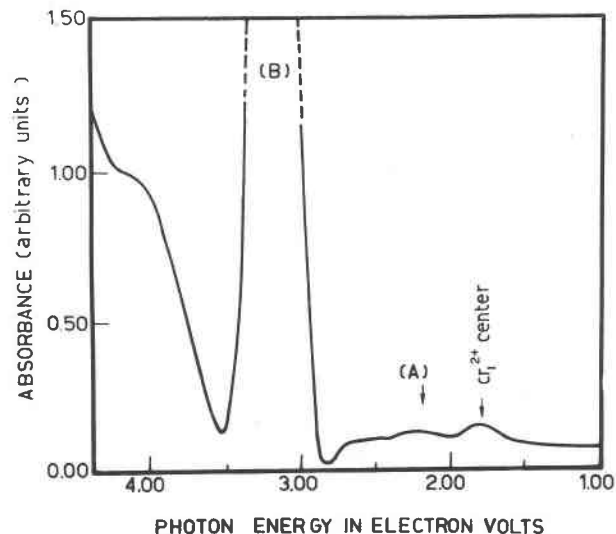
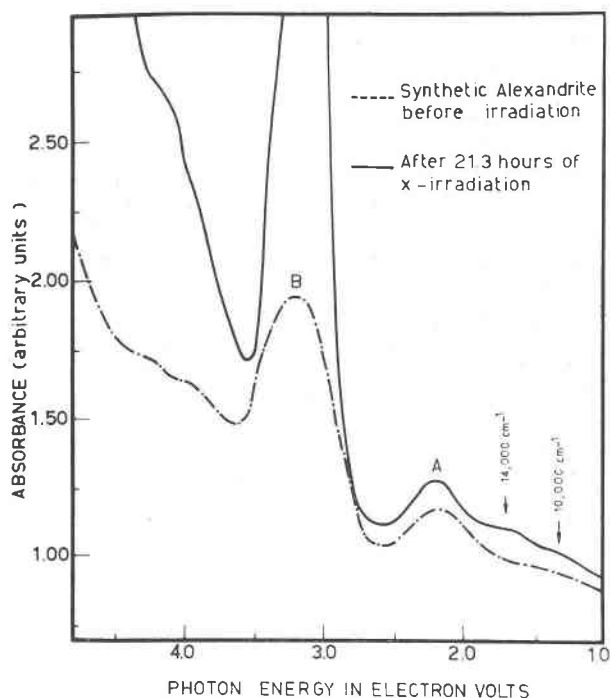FIG. 7. Difference in absorbance of synthetic alexandrite before and after 21.3 hours of X-irradiation.

FIG. 8. Optical absorption spectra of X-irradiated synthetic alexandrite (————), and after heating at 500°C for 2 hours (— — —).

thus the spectrum. We may reach the same condition by changing the pressure. Under higher pressure, the Cr^{3+} ions are squeezed, a condition which is capable of altering the color.

Conclusions

The color and the color-change phenomenon characterizing synthetic alexandrite crystals result from the presence of Cr^{3+} in distorted octahedral sites.

The results reported in this investigation suggest that the Cr^{3+} ions substitute for the Al^{3+} ions in the structure in two different sites that differ significantly in size and symmetry: the $Cr^{3+}(1)$ sites and the somewhat larger $Cr^{3+}(2)$ sites. The $Cr^{3+}(1)/Cr^{3+}(2)$ population ratio is believed to influence the color exhibited by the crystal and the degree of the color-change phenomenon. The color sensation which the alexandrite produces depends on the intensity distribution of the light sources. Daylight, or any similar white radiation with normal distribution of wavelengths, interacts normally with the two Cr^{3+} centers imparting both the green color and the reddish tint depending on the $Cr^{3+}(1)/Cr^{3+}(2)$ population ratio; the higher the $Cr^{3+}(1)/Cr^{3+}(2)$ ratio, the more reddish the tint imparted by the crystal. In incandescent

light, which is relatively poor in shorter wavelengths, alexandrite exhibits a deep purplish-red color. The existence of the intense B band absorbing in the blue would filter out most of the wavelengths in this region (up to about 2.8 eV), so that the broad absorption in the $A_{complex}$ band region mostly controls the transmitted radiation. The wavelengths absorbed by the $A_{complex}$ band happen to be mainly the green. Due to the breadth resulting from the complex nature of the A band, part of the bluish green and of the yellowish green radiation (spectral region 1.9–2.4 eV) is also absorbed; this allows the complementary purplish red radiation to be exhibited. The smaller the $Cr^{3+}(1)/Cr^{3+}(2)$ population ratio, *i.e.*, the more concentrated the $Cr^{3+}(2)$ centers are, the more significant will be the absorption effect of the $A_{complex}$ band.

The idea that V^{3+} may play a role in the color-change phenomenon can be considered at this point. It is known that the first spin-allowed electronic transition in the partially filled $3d$ shell of the V^{3+} ion absorbs in the same spectral region as the $A_{complex}$ band; so that the $A_{complex}$ band can be made broader and more intense by introducing trace V^{3+} (found to be present in the investigated specimen). However, it should be made clear that the $A_{complex}$ band is neither the only nor the main factor there; the number of absorbing centers in the B band region is as important and must reach a certain value to filter out completely the shorter visible wavelengths, which are already of low intensity in incandescent radiation. The B band happens to be more intense relative to the A band in pink Cr^{3+} compounds (Table 2). Small concentrations of $Cr^{3+}(1)$ centers are sufficient to increase the absorbance in the B band as compared to that in the $A_{complex}$ band region. It is felt that if Cr^{3+} ions are introduced in the crystal so that a certain critical value of the $Cr^{3+}(1)/Cr^{3+}(2)$ population-ratio is obtained, the color-change phenomenon will be exhibited. This is definitely dependent on the process of growing the crystal. The $Cr^{3+}(1)$ centers are expected to enter the structure either at very high temperatures and normal pressures or at high pressures with the temperature not as high. This point needs further detailed investigation in which host crystals having the same composition would be allowed to grow with different concentrations of Cr^{3+} at different temperatures and pressures. If established, the population ratio, $Cr^{3+}(1)/Cr^{3+}(2)$, might serve as a criterion for knowing the history of chromium-bearing alumina-minerals and

serve as an excellent geothermometer as well as a geobarometer.

Acknowledgments

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