

THE AMERICAN MINERALOGIST, VOL. 52, MAY-JUNE, 1967

THE "ALEXANDRITE EFFECT": AND OPTICAL STUDY

WILLIAM B. WHITE¹, RUSTUM ROY¹, AND J. MCKAY CRICHTON*Materials Research Laboratory, Pennsylvania State
University, University Park, Pennsylvania.*

Alexandrite ($\text{Al}_{2-x}\text{Cr}_x\text{BeO}_4$), a variety of chrysoberyl, is valued as a gem stone because of its unique optical properties. Its striking and characteristic property is a change from a green color to a reddish purple in different environments. The origin of this color change is often attributed, quite erroneously, to dichroism. Simple observation shows that the change depends chiefly on the nature of the incident light. In antiquity this change was from sunlight to (presumably) candlelight and this exhibition is still used today by many gemologists and jewelers. Striking effects are also observed when the change is from a (blue) fluorescent light to incandescent lighting (low-color temperature). It was this striking color change in a ring when moved from the jewelers' case to sunlight that drew our attention to this matter. Natural alexandrite is a crystalline solution of Cr^{3+} in Al_2BeO_4 . In general it is not even known what the host structure in the *synthetic* "alexandrite" is: indeed the manufacturer's laboratory was not sure whether it was spinel or alumina. This study was aimed at understanding the nature of the crystal field environment giving rise to this rare optical effect. After most of our study was complete, Farrell and Newnham (1965) published the optical spectra of natural and synthetic alexandrite and have shown, as we had, quite clearly that the color and pleochroism are due to the presence of Cr^{+++} in a distorted octahedral site. It is the purpose of this note to add two additional comments to Farrell and Newnham's interpretation. One is to elucidate further the nature of the visual color change; the second is to point out that such a color-change phenomenon is not a unique property of the mineral alexandrite nor of the Cr^{+++} ion.

Most chromic compounds are either pink or green. In a few series of crystalline solutions, for example, the ruby ($\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$) series, the color may be either pink or green depending on the chromium concentration but there has been no report of a color change with change in incident lighting. One should remember that while the energy levels of the Cr^{+++} ion determine the maxima in the absorption spectrum, the observed color is determined chiefly by the *minima*. Chromic compounds have two such minima, one between the absorption bands and one on the long wavelength end of the spectrum. The wavelengths of the absorption bands are

¹ Also associated with the Department of Geochemistry and Mineralogy.

a function of the strength of the crystal field of the coordination octahedron surrounding the Cr^{+++} ion. As the field changes, the band positions and thus the location of the minima shift and the color changes *slightly*. The red-green color change in Cr^{+++} compounds however is more drastic and *not* continuous. As is well known, green compounds remain green with decreasing chromium content until at a critical concentration the color abruptly becomes pink with only a short range of neutral gray.

Poole (1964) has made a very careful study of the color changes in some 70 chromium compounds by means of tristimulus analysis and has reached the conclusion that the color change is due to what he calls a "psycho-physical" effect. That is, the color change is due to the response of the human eye and brain and not to any abrupt changes in the properties of the material. As the chromium composition moves from those values which yield green compounds to those values which yield pink compounds, the interband minimum in the spectrum moves from near $525 \text{ m}\mu$ toward shorter wavelengths. The eye is very sensitive to green light and is less sensitive to red and blue so it responds most strongly to the green light and the compound appears green. As the light passed by the interband minimum becomes more blue and the light passed by the long wavelength minimum becomes brighter red, the eye shifts its response from predominantly the green stimulus to a mainly red stimulus with some blue component. The material now appears pink. It appears certain that the physiological response of the human eye in a *particular* part of the visible spectrum is also responsible for the change of color in alexandrite. We therefore propose the term "Alexandrite Effect" to describe the phenomenon of an observed color change from greenish to reddish with a change in source illumination.

Five natural alexandrites (Al_2BeO_4) were examined. In two of these five the color-change with incident lighting change was very much more marked than in the others. Electron probe analysis for the Cr-content showed that the concentration was near 0.18 mole percent Cr_2O_3 for the materials showing no change and 0.64 mole percent for those showing a definite change. The explanation for this must lie in the fact that in order for the "change" to be observed, the optical absorption must be sufficiently high within the bands not to permit too much transmission "under" the bands.

Moreover, if this general theory of the alexandrite-effect is correct it should *not* be a rare phenomenon, and indeed should be observed in many materials. The most obvious of these, of course, is the Al_2O_3 - Cr_2O_3 series mentioned above, which goes from the characteristic ruby to the bright green of Cr_2O_3 . This behavior has been recently reexamined in some detail in the ruby Cr_2O_3 series by Barks, Roy and White (1965). The color change takes place very abruptly near 20 wt. percent Cr_2O_3 . The measured

lattice parameters and crystal field parameters were shown to be continuous functions of composition and have no discontinuities whatsoever at the color change point.

Further examination showed that single crystal material with 20 wt. percent Cr_2O_3 appears distinctly pink when viewed in incandescent light and distinctly green when viewed in daylight. Only rubies with compositions near the critical composition exhibit this effect.

Furthermore, since the alexandrite effect is shown to be due only to critical wavelength minima in the absorption spectrum, there is no reason why this effect should be limited to chromium compounds. Indeed, it is not and one additional example is given here. Many commercial gem mineral supply houses sell what they call synthetic alexandrite. These are

TABLE 1. EMISSION SPECTROGRAPHIC ANALYSES OF ARTIFICIAL ALEXANDRITE

	Crystal A (wt. %)	Crystal B (wt. %)
Fe_2O_3	1.2	n.d.
MnO	0.03	n.d.
TiO_2	0.01	n.d.
V_2O_5	0.45	0.55

Not detected (n.d.): Co, Ni, Cu, Zn.

typical corundum boules which exhibit an alexandrite-like color change which is even more dramatic than that of most natural stones. Two of these boules were examined. An emission spectrographic analysis is given in Table 1 and the absorption spectrum of the A-boule is given in Figure 1. It is clear therefore that the active element in synthetic "alexandrite" is vanadium, present as V^{+++} . The position of the two absorption peaks agrees well with the bands observed by McClure (1962) and there seems to be little doubt about the assignments. V^{+++} like Cr^{+++} has an F -ground state and gives rise to three spin-allowed bands, two of which appear in the visible part of the spectrum. The two absorption minima are at 490 and 680 μ compared to Farrell and Newnham's value of 490 and 670 μ for natural alexandrite. Any ion or combination of ions whose spectrum had minima at these critical values would presumably give a similar effect.

One might ask whether an alexandrite—type color effect could be generated by Ni^{++} or Co^{++} in minerals since these ions also have F -ground states. The answer is that it is not likely. V^{+++} and Cr^{+++} as trivalent ions have crystal field splitting parameters of 1750 and 1815 cm^{-1} respectively in corundum. Ni^{++} and Co^{++} as divalent ions have Dq values of 860 and 1000 cm^{-1} which reduces the splitting of the energy levels, moves the

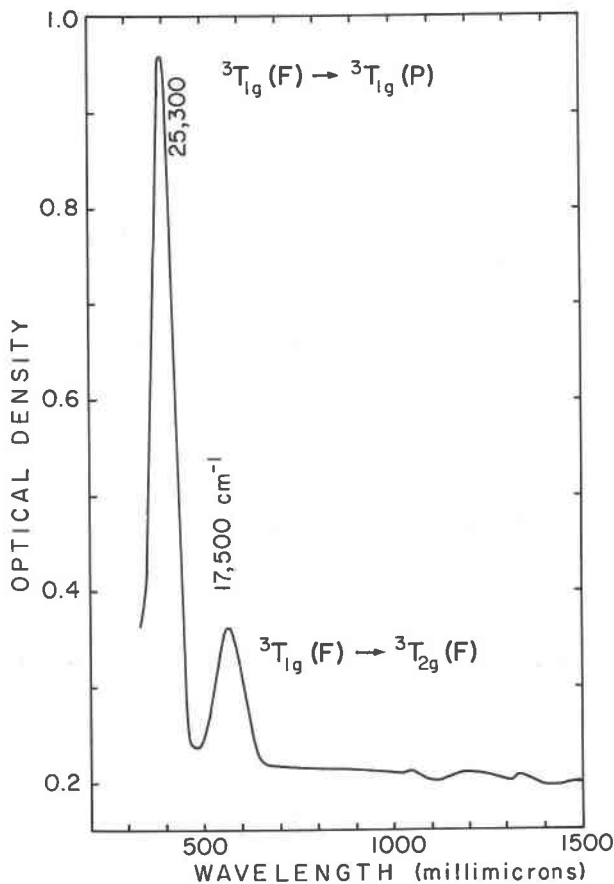


FIG. 1. Absorption spectrum of V^{+++} in corundum (synthetic alexandrite).

absorption bands toward the infrared and makes it very unlikely that the absorption minima could have critical values. Alternatively one could conceive of preparing appropriate mixtures of ions which might permit such a critical window to be generated.

ACKNOWLEDGEMENT

Research on the optical spectra of crystals is supported by the National Science Foundation under Grant No. GP-3232.

REFERENCES

- BARKS, R. E., D. M. ROY AND W. B. WHITE (1965). Sub-solidus equilibria in the system $Al_2O_3-Cr_2O_3$ and optical spectra of the crystalline solutions. *Bull. Amer. Ceram. Soc.* **44**, 317.

- FARRELL, E. F. AND R. E. NEWNHAM (1965). Crystal field spectra of chrysoberyl alexandrite, periodit, and sinhalite. *Amer. Mineral.* **50**, 1972-1981.
- McCLURE, D. S. (1962) Optical spectra of transition-metal ions in corundum. *J. Chem. Phys.* **36**, 2757-2779.
- POOLE, C. P., JR. (1964). The optical spectra and color of chromium-containing solids. *J. Phys. Chem. Solids* **25**, 1169-1182.

THE AMERICAN MINERALOGIST, VOL. 52, MAY-JUNE, 1967

X-RAY STUDY OF SIX-LAYER ORTHO-SERPENTINE

I. KRSTANOVIĆ, *Department of Geophysical Sciences, University of Chicago, Chicago, Illinois*¹ and S. PAVLOVIĆ, *Department of Mineralogy and Crystallography, University of Beograd, Beograd, Yugoslavia.*

Of all the serpentine minerals, the six-layer ortho-serpentine is least well characterized. It was originally described by Brindley and von Knorring (1954) with additional data given by Zussman, Brindley and Comer (1957), Zussman and Brindley (1957) and by E. Olsen (1963). It has been synthesized by Roy and Roy (1954) and by Gillery (1959). The structure of the mineral is not known and reports on the mode and the frequency of occurrence are scarce. During the investigation of the mineralogical composition of the well-developed serpentinite bodies in Yugoslavia. The mineral was found to be the main constituent of the black serpentinite that occurs as lenses in the Paleozoic schists at Korab Mt. As a pure component it forms thin sheets or lenses interbedded with asbestos veins in the same region. It is inferred from the scarcity of secondary magnetite grains that the rocks prior to serpentinization consisted mainly of high-magnesian olivine. The mineral is a main constituent of a large body of serpentinitized dunite at Radusa mine. It is always found in regions where serpentinite rocks have been altered hydrothermally.

X-RAY INVESTIGATION

Powder data were obtained from a 19 cm. camera using Cu (Ni-filtered) radiation, and fiber photographs were taken in a 6 cm. camera. A fiber photograph of a specimen whose powder pattern is given in column 3 of Table 1, and which is a pure six-layer ortho-serpentine, shows sharp reflexions on all layer lines which are, however, elongated along Debye arcs. On the zero layer line 00l, 0k0 and a few 0kl reflexions were

¹ Present address: Department of Mineralogy and Crystallography, Faculty for Mining and Geology, University of Beograd, Beograd, Yugoslavia.