Relationship between the crystallographic orientation and the 'alexandrite effect' in synthetic alexandrite

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Abstract

The transmittance spectra of a synthetic alexandrite recorded along directions parallel to the three crystallographic axes are generally similar, but the observed colour changes along these directions under different light sources are quite different. Calculated hue-angle changes for the colours observed under different pairs of C.I.E. standard illuminants are the largest for light travelling parallel to the *a*-axis. Therefore, alexandrite should be cut as a gemstone with the top facet oriented parallel to (100) for it to show the most dramatic change in colour.

KEYWORDS: chrysoberyl, alexandrite, alexandrite effect, colour.

Introduction

IN 1830 a new gem material with a conspicuous change of colour when viewed under different light sources was found in the Ural Mountains of Russia (Wörth and Perovksy, 1842). Named 'alexandrite' for the then-future Tsar Alexander II, the material proved to be a Cr-bearing variety of the mineral chrysoberyl that is green or bluish-green in daylight, and red or purplish-red in incandescent light. This dramatic change in colour appearance has resulted in the continued popularity and high value of alexandrite as a gemstone. This kind of colour change is now referred to as the 'alexandrite effect' (White *et al.*, 1967; Schmetzer *et al.*, 1980). Both Farrell and Newnham (1965), and Hassan and El-Rakhawy (1974) attributed it in part to the characteristic spectrum of both natural and synthetic alexandrite which contains two broad absorption bands due to Cr^{3+}.

Chrysoberyl is orthorhombic, and its optical properties differ along the three crystallographic axes. As such, the colour change displayed by alexandrite should vary with optic orientation. Crystals of natural gem alexandrite are faceted to retain the greatest possible weight, and not with any attempt to orient them optically to show the best colour change. This study, part of a larger investigation of gemstones exhibiting the alexandrite effect, was undertaken to establish the relationship between the crystallographic orientation and intensity of the colour change in alexandrite.

Experimental

Natural gem alexandrites are difficult to obtain because of their great rarity and resulting high value. Such crystals may exhibit (100) and (001) faces, and rarely, small (010) faces (the latter not present on crystals in GIA's collection). Synthetic alexandrite, grown by a variety of methods, is an important laser material and is more readily available. This is why, in this study, we used a sample of synthetic alexandrite grown from a melt of stoichiometric composition by the Czochralski technique (Bukin *et al.*, 1981). This sample was polished in the form of a cube, with each surface perpendicular to a crystallographic axis (Fig. 1). The crystallographic orientation of the three surfaces of the polished cube was established by X-ray diffraction using a Scintag XPH-105 diffractometer. Transmittance spectra were recorded with an Hitachi U4001 spectrophotometer (with an integrating sphere) for directions along the three crystal-

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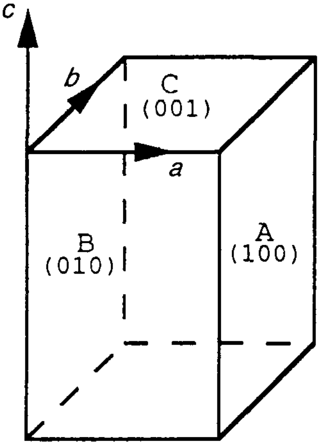

FIG. 1. The synthetic alexandrite sample used in this study measures 7.61 × 7.83 × 10.34 mm. The cube was polished such that surface A is (100), B is (010), and C is (001).

lographic axes of the sample. The sample was positioned at the entrance of the integrating sphere, with the unpolarized incident light focused on the sample's surface. Therefore, the three recorded spectra are 'directional' spectra corresponding to what an observer might see, and are not polarized spectra. For this reason, the spectra are appropriate for colorimetric calculations. Calculations of colour hue (h) and hue-angle change (Δh) were carried out using the resultant transmittance spectra, a modified Spectra-Calc software program, and C.I.E. standard illuminants A, D65, and F7 (C.I.E. Colorimetry, 1986). As a check on the colorimetric data, the colour hues of the sample along the three crystallographic axes were also observed separately under incandescent, D65 xenon 'daylight simulator', and fluorescent 'daylight simulator' light sources that correspond to these three C.I.E. illuminants (Table 1).

TABLE 1. Colours observed visually along the three crystallographic axes of the synthetic alexandrite

Axis	Observed hue		
	I	D	FD
a	Reddish purple	Green	Green
b	Purple	Blue	Blue
c	Bluish Green	Green	Green

Note: Light sources for the observed hues are: I – incandescent light, D – xenon 'daylight simulator', FD – fluorescent 'daylight simulator'.

Results

The three transmittance spectra of the synthetic alexandrite have generally similar shapes (Fig. 2). Two broad absorption bands occur — one extending up to about 450 nm, and the other centred at about 560 nm. These bands separate two regions of transmission — one between about 450 and 550 nm, and the second starting between 600 and 650 nm (Fig 2., spectra A to C). These same features, and the fact that they are offset slightly from one another if the spectra are recorded with polarized light along the three crystallographic directions, were reported by Farrell and Newnham (1965).

Table 2 presents the results of the calculations in CIELAB colour space of both the hue angles (h) for each of the C.I.E. standard illuminants, and hue-angle changes (Δh) for pairs of these three illuminants. The fact that different hue angles are calculated for the same crystallographic direction means that different colour hues are being measured along the same direction for these three standard illuminants. Comparison of the data in Tables 1 and 2 indicates agreement in both the observed and calculated colour hues and hue-angle changes.

TABLE 2. Calculated colorimetric data for the synthetic alexandrite sample along the three crystallographic axes

Axis	Hue-angle (h)			Hue-angle change (Δh)		
	A	D65	F7	Δh1 (A-D65)	Δh2 (D65-F7)	Δh3 (A-F7)
a	335	162	152	173	10	177
b	299	240	233	59	8	66
c	233	167	164	66	3	69

Note: h is the hue angle (in degrees), Δh is the hue-angle change, (A-D65) means the difference under C.I.E. standard illuminants A and D65, (D65-F7) the difference under illuminants D65 and F7 and (A-F7) the difference under illuminants A and F7.

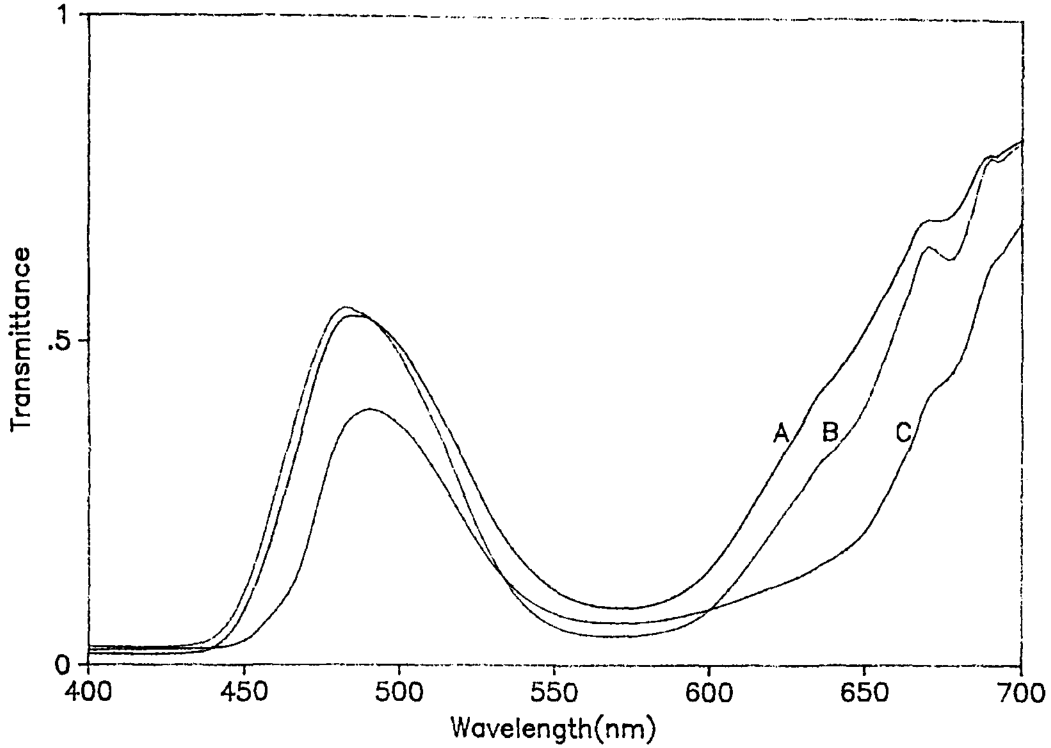

FIG. 2. Transmittance spectra recorded over the wavelength range 400–700 nm for directions along the *a*-, *b*-, and *c*-axes of the polished cube sample of synthetic alexandrite (Spectra A, B, and C, respectively).

Discussion

Liu *et al.* (1994) demonstrated that the alexandrite effect in gemstones can be quantitatively judged by calculating the absolute hue-angle change (Δh) between pairs of C.I.E. standard illuminants. If this change is greater than 20°, we would expect to observe a colour change when the gem is viewed under the corresponding pair of light sources.

As shown in Table 2, the greatest hue-angle change for the synthetic alexandrite sample occurs between illuminant pairs (A-D65) and (A-F7). For these two pairs, the largest Δh is for light travelling parallel to the *a* crystallographic axis (a change of almost 180°, that is, almost opposite colours in the hue circle in CIELAB colour space). The hue-angle changes for light travelling parallel to the *b*- or *c*-axes are still sufficient to be viewed by the eye as a change in colour, but the change will be much less dramatic, and also, less attractive. This difference in colour change is in spite of the general similarity of the three transmittance spectra shown in Fig. 2. Comparison of these spectra reveals a difference in intensity of the 450–550 nm transmittance band, but more importantly, a significant shift in the wavelength position of the edge of the transmittance band starting above 600 nm. It is our experience that the visible spectra of both natural and synthetic alexandrite are similar. Therefore, these results can be applied to natural alexandrites as well.

Conclusion

This study has demonstrated that synthetic alexandrite exhibits its greatest colour change for light travelling parallel to the *a* crystallographic axis. To display the best 'alexandrite effect', the 'table' facet (the largest polished surface on the top of a gemstone) of an alexandrite should be oriented as closely as possible to (100). Fig. 3 presents drawings of untwinned and twinned chrysoberyl crystals showing the orientation of the table facet of a cut stone, with, respect to the original crystal shape, that will exhibit the best blue-green to red colour change for alexandrite.

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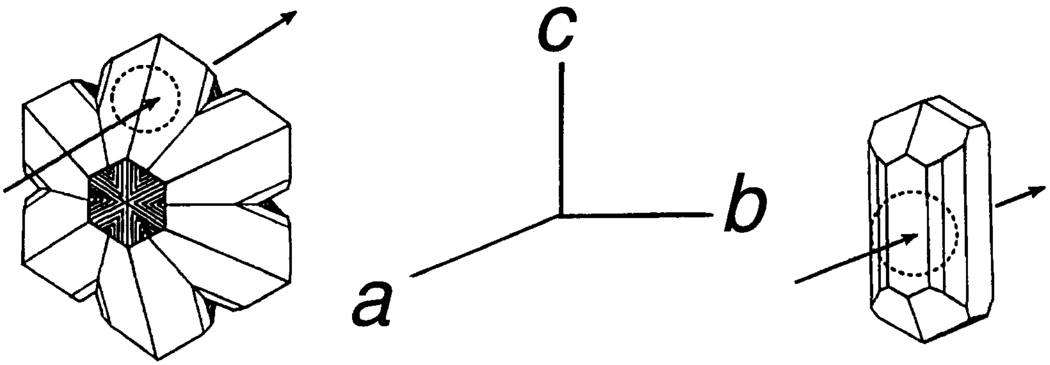

FIG. 3. Morphology of twinned and untwinned natural chrysoberyl crystals with the orientation of the table facet (indicated by a dashed line) that will display the best colour change in a faceted alexandrite. Redrawn from Goldschmidt (1913).

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References

Bukin, G. V., Matrosov, V. N., Orekhova, V. P., Remigailo, Y. L., Sevastyanov, B. K., Syomin, E. G., Solntsev, V. P. and Tsvetkov, E. G. (1981) Growth of alexandrite crystals and investigation of their properties. *J. Cryst. Growth*, **52**, 537–541.

Commission Internationale de l'Eclairage (C.I.E.) (1986) *Colorimetry*, 2nd Edition. Publication No. 15.2, Vienna.

Farrell, E. F. and Newnham, R. E. (1965) Crystal-field spectra of chrysoberyl, alexandrite, peridot, and sinhalite. *Amer. Min.*, **50**, 1972–81.

Goldschmidt, V. (1913) *Atlas der Krystallformen*. C. Winters Universitätsbuchhandlung, Heidelberg.

Hassan, F. and El-Rakhawy, A. (1974) Chromium III centers in synthetic alexandrite. *Amer. Mineral.* **59**, 159–65.

Liu, Y., Shigley, J. E., Fritsch, E. and Hemphill, S. (1994) The 'alexandrite' effect in gemstones. *Color Res. Appl.*, **19**, 186–92.

Schmetzer, K., Bank, H. and Gübelin, E. (1980) The alexandrite effect in minerals: chrysoberyl, garnet, corundum, fluorite. *Neues Jahrb. Mineral., Abh.*, **138**, 147–64.

White, W. B., Roy, R. and McKay-Crichton, J. (1967) The 'alexandrite effect': an optical study *Amer. Mineral.*, **52**, 867–71.

Worth, F. I. and Perovsky, L. A. (1842) Über Alexandrit und Chrysoberyll. *Verhandlung Russ.-Kaiserl. Mineral. Ges.* St. Petersburg, Vol. 1, No. 1, (not seen; cited in J. Sinkankas, *Gemology — An Annotated Bibliography*, Vol. **2**, p. 1145, Scarecrow Press, Metuchen, New Jersey, 1993).

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