# An optical criterion to obtain miscible mixed crystals in alkali halides

R. Rodríguez-Mijángos[a], G. Vázquez-Polo[b], J.J. Palafox*, and R. Pérez-Salas[a]
[a] *Centro de Investigación en Física, Universidad de Sonora,*
*Apartado Postal 5-88, 83190, Hermosillo, Sonora, México.*
[b] *Instituto de Física, Departamento de Estado Sólido, Universidad Nacional Autónoma de México*
*Apartado Postal 20-364, 01000, México, D.F.*
** Departamento de Geología, Universidad de Sonora,*
*Rosales y Colosio, 83000, Hermosillo, Sonora, México.*

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This work gives a novel criterion to predict the formation of alkali halide solid solutions and discusses some results obtained in the development of ternary and quaternary miscible crystalline dielectric mixtures of alkali halides. These mixtures are miscible in any concentration of their components. The miscibility of these mixed crystals is quite related to the F center through the behavior observed in the spectral position of the optical absorption F band as a function of the lattice constant of the alkali halide where the F center was formed. By inspection of an energy graph of the F band energy versus lattice constant (Mollwo-Ivey law), a set of points is observed corresponding to several pure alkali halides (such as KCl, KBr, RbCl), which gives a notion of possible mixed materials that would correspond to adjacent points and a solid solution could be obtained, meaning a single phase crystal, which result in ternary and quaternary mixed crystals. Thus, the optical absorption F band allows have a numerical criterion, based on the percentage respective of the F band energy, in order to predict possible solid solutions. We obtained experimental information using diffractograms of the mixed crystals, from which the lattice constant was obtained and compared with a theoretical calculus using a generalization of Vegard's law, finally it is discussed the case of a crystal growing, starting from five components, picking up five consecutive dots from the graph of Mollwo-Ivey's law.

*Keywords:* F center; solid solutions; optical properties; dielectric mixtures; defects in alkali halides crystals.

Este trabajo ofrece un nuevo criterio para predecir la formación de soluciones sólidas en halogenuros alcalinos cristalinos y discute algunos resultados obtenidos en el desarrollo de mezclas dieléctricas cristalinas miscibles de halogenuros alcalinos ternarias y cuaternarias. Estas mezclas son miscibles en cualquier concentración de sus componentes. Tener el resultado de estas mezclas cristalinas está relacionado al centro F a través del comportamiento observado en la banda F de absorción en función de la constante de red de los halogenuros alcalinos dónde el defecto fue formado (centro F). Dando un vistazo a la gráfica de Energía de banda F versus constante de red (ley de Mollwo-Ivey), se observa un conjunto de puntos, que dan la pauta (tal como KCl, KBr, RbCl), de posibles mezclas de materiales correspondientes a puntos adyacentes y una solución sólida podría formarse, significando un cristal de una sola fase, que dan por resultado cristales ternarios y cuaternarios. Así, la banda F de absorción nos permite tener un criterio numérico, basado en el porcentaje de cambio de la energía de la banda F que permite obtener soluciónes sólidas.. Encontramos información experimental, usando difractogramas de las mezclas cristalinas, se obtienen las constantes de red y se comparan con la obtenida teóricamente a través de la generalización de la Regla de Vegard, finalmente se discute la posibilidad de crecer cristales partiendo de cinco componentes, tomando cinco puntos consecutivos en la gráfica de la Ley de Mollwo-Ivey.

*Descriptores:* Centro F; soluciones sólidas; propiedades ópticas; mezclas dieléctricas; defectos en halogenuros alcalinos cristalinos.

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## 1. Introduction

The first dielectric materials and, in particular, the first materials studied by X-ray diffractometry were the alkali halides, particularly NaCl. Its study was simplified because of its face-centered cubic (fcc) structure, which is currently well known, and is the standard for the study of materials of more complex structure. A similar situation happened with the study of crystalline defects, the study of an electron trapped inside a halide vacancy, which is the F Center defect that is formed by irradiation a crystalline alkali halide, or by additive coloration, immersing the crystal under alkali metal vapor. Understand the F center allowed to open the study field of defects in other materials different to alkali halides.

The first systematic miscible binary crystalline mixtures study of alkali halides was conducted by Smakula in the mid-$20^{th}$ century [4]. According to their X-ray diffractograms, they present an fcc crystalline structure, which is similar to their components. The peaks of the typical diffractogram appear at different reflection angles, following Bragg's law, and depending on the concentrations of their components.

The perfect relation that exists when there is perfect miscibility between two alkali halides with an fcc structure to form another similar structure was discovered by L. Vegard and H. Schjelderup in 1917 in a mixture of KCl:KBr [5]. Shortly after, L. Vegard experimentally confirmed that the lattice constant of the newly formed crystal is the weighted average of the lattice constants of its components that is [5]:

$$a = a_1 X_1 + a_2 X_2 \tag{1}$$

where $a$ is the lattice constant of the mixture, and the addend is formed by the product of the lattice constants $a_1$, and $a_2$, and the corresponding $X_1$ and $X_2$ molar fraction of its components. Currently, this Eq. (1) is known as Vegard's Law

and it has been found that it is valid for all crystalline materials of cubic symmetry. The probably most studied mixture is $KCl_XKBr_{1-X}$, where X and 1- X are the respective molar fractions.

Crystal defects play an important role in physics and chemistry of crystals. The first systematically studied defect was the F center in alkali halides. This study was launched in Germany by Pohl in the 1920's. It was discovered that pure and as grown alkali halide crystals being transparent became colored when were irradiated with X-rays. By the time he was not sure what the defect consisted of. Many years later it was determined, mainly, thanks to experimental evidence of paramagnetic resonance [3], that the F Center is an electron trapped in a halide vacancy.

There is an experimental correlation between the F band peak energy and lattice constant [3], which we will show in this work. This will allow us to obtain a new miscibility criterion different from the traditional one, and us to predict the possibility of having ternary and quaternary mixtures as single-phase alkali halide crystals. The criterion established in the literature for miscibility between two components is that the relative difference between their respective lattice constants does not exceed 8%. Exceptionally, it has been reported that this percentage can reach 10%. All the binary mixtures studied by Smakula agree with the this empirical criterion [4].

The aim of this paper is to prove that with the arguments mentioned above, and by using a chart of the F band peak energy vs. lattice constant, a KCl:KBr:RbCl type ternary crystal can be grown as a solid solution, in which the F band absorption, as well as its diffractogram, must reflect the crystalline characteristic of having a single phase [1]. In the same way, other ternary and quaternary crystals can be obtained, as will be described in the following sections. The F band will allow us an optical criterion of miscibility, based on its percentage change in the mixed components, an alternative to the traditional criterion

## 2. Experimental

All of the ternary and quaternary mixtures were grown at the Laboratorio de Crecimiento de Cristales del Instituto de Fisica de la UNAM (Crystal Growth Laboratory of the Physics Institute, UNAM), mixing three or four alkali halides, by using the Czochralski method. In general, the growths were achieved with molar fractions of the different salts of the mixture proposed, in some cases adding an impurity at trace levels such as $EuCl_2$, because Europium allows the study of interesting optical properties. Several studies of the optical properties were conducted in the Laboratorio de Estado Solido del Centro de Investigación en Física de la Universidad de Sonora (Solid State Laboratory of the Physics Research Center of the University of Sonora) [6]. In general, the grown mixtures were recognized as single-phased, because when removed from the growing furnace they were perfectly transparent. To obtain diffraction diagrams of several crystals, a latest-generation Bruker diffractometer was used at the Laboratorio de Cristalografía y Mineralogía del Departamento de Geología de la Universidad de Sonora (Laboratory of crystallography and mineralogy of the department of Geology of the University of Sonora) [7]. The X-ray diffraction study of the first ternary crystal was done in the Laboratorio de Rayos X del Instituto de Física de la UNAM (Laboratory of X-Rays of the Physics Institute, UNAM) [1].

## 3. Results

The first ternary crystal to be characterized was KCl:KBr:RbCl in equal molar fraction (X=0.33) [1] for each of its components. Figure 1, observed below, presents on a logarithmic scale the energy peak of the F band vs. the lattice constant of several alkali halides. The empirical relation derived from this graph is the Mollwo-Ivey law [3]. In the graph, we see the points associated with KCl, KBr and RbCl are very close to each other, leading to conjecture the existence of the ternary crystal. That the measured energy of the F band corresponds to another ternary crystal already studied, $KCl_xKBr_yRbBr_z$ (x= 0.5, y= 0.25, z= 0.25), its difractometry is shown in Fig. 2, the registered F band is simple [7], and according with the diffractogram, has a well defined lattice parameter, in agreement with a Vegard's generalized law.

From the same Fig. 1, one can see that next to the three points corresponding to KCl, KBr and RbCl is another one corresponding to RbBr. This suggests that others ternary crystals could be formed, substituting RbCl by RbBr and, moreover, mixing four salts, the bromides KBr and RbBr and the chlorides KCl and RbCl, respectively, a single-phase quaternary crystal could be formed. If that were to happen, the crystal that was formed would be a KCl:KBr:RbCl:RbBr type solid solution proportional to the mole fraction [9]. Its difractogram is shown in Fig. 3.

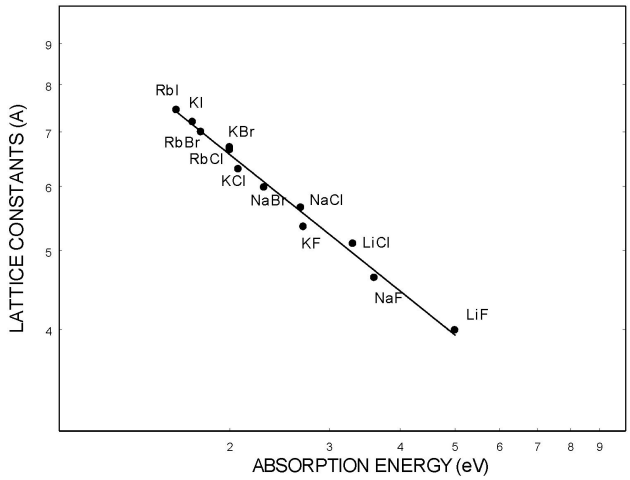


FIGURE 1. Position of peak of F band absorption in electron volts (eV) according to lattice constant in angstroms (A) (vertical axis) for several alkali halides [7].

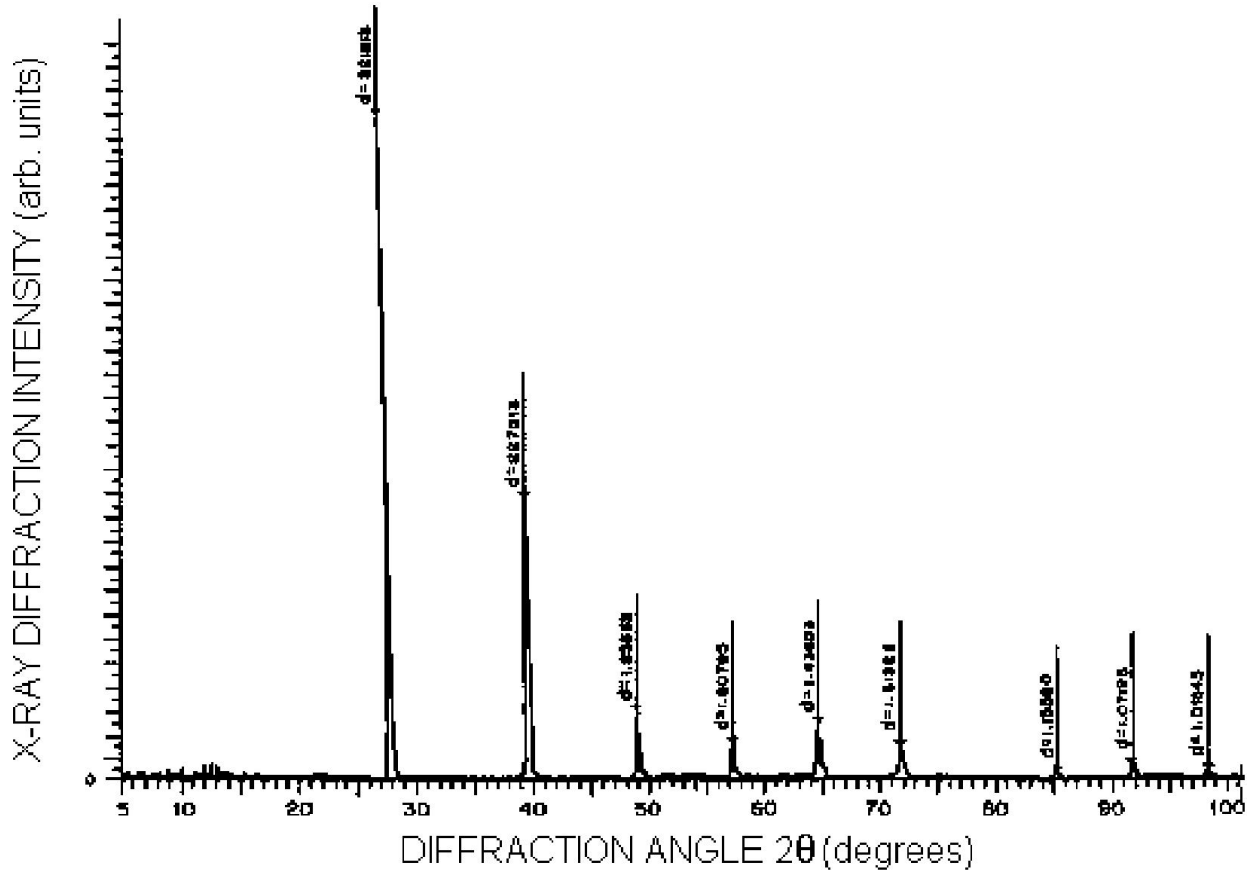


FIGURE 2. Difractometry of the ternary crystal KCl:KBr:RbBr (0.50:0.25:0.25**)**.

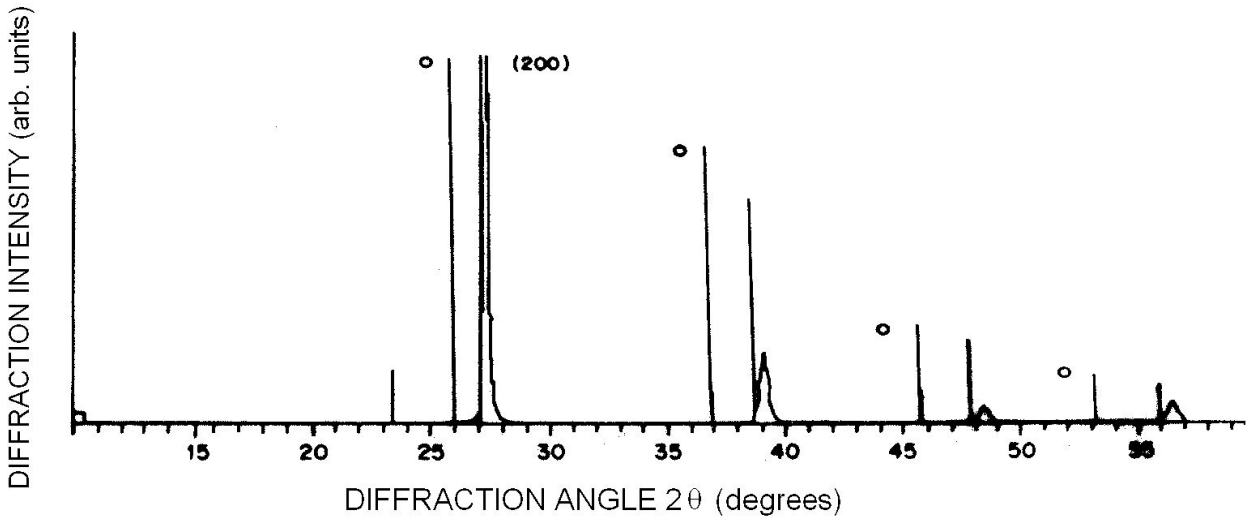


FIGURE 3. Difractometry of the quaternary crystal with equal molar composition.

Another ternary crystal has been grown [7,10], with the same components of the former one [6], but with a different molar fraction given by x = 0.5 for KCl and y=z=0.25 for KBr and RbCl, respectively. All the ternary and the quaternary materials follow what is called generalized Vegard's Law [1], similar to the Vegard Law given by the Eq. (1). When dealing with ternary and quaternary crystals, a generalized Vegard's Law will have three and four addend, respectively, that will determine the lattice constant of the new material, a lattice parameter weighted average obtained from the sum of the products of the corresponding molar fractions and lattice constants of the mixture components.

TABLE I. Peak energy values of the optical absorption band of the F Center (F band: EF ) in electron Volts (eV) and the values of the corresponding lattice constant in Angstroms (A), of the four alkali halides used to form ternary and quaternary single-phase crystals. The table also shows the EF values of the following crystals with largest lattice constant [3].

| Crystal | EF (eV)* | a (A)** |
|---|---|---|
| KCl | 2.313 | 6.2931 |
| KBr | 2.064 | 6.60 |
| RbCl | 2.050 | 6.581 |
| RbBr | 1.857 | 6.889 |
| KI | 1.875 | |
| RbI | 1.708 | |

* Ref. [3]; ** Ref. [15]

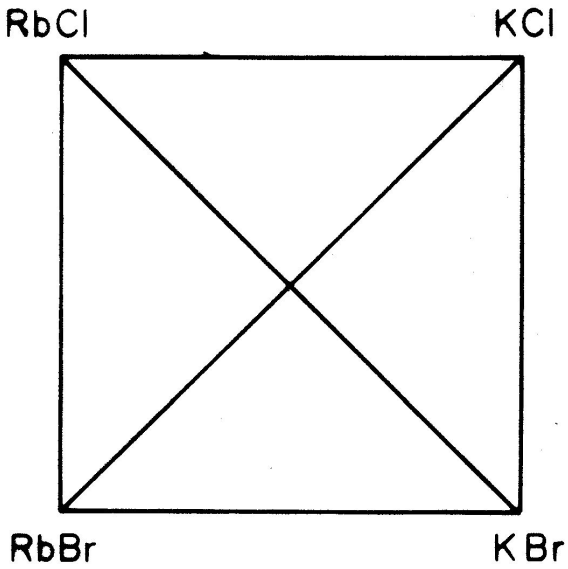


FIGURE 4. Geometrical representation of the crystallographic family. At the left, salts with heavier ions.

Given the relatively large number of combinations of the quaternary crystal components, we can suppose that these crystals can be obtained in any composition, forming single-phase fcc crystals. For example a quaternary crystal was grown with X = 0.10 for KCl and a concentration of 0.30 for each of the other three components (KBr, RbCl and RbBr). The expected fcc crystal was obtained, also satisfactorily complying with the generalized Vegard's Law since the weighted average value coincides with the experimental value obtained by X-ray diffractometry [8]. Table I presents the peak energy values of the F band and the lattice constants of the single crystals, and Table II, the experimental and theoretical values of the mixed crystals studied. The percentage variation between the smallest and the largest lattice constants is 10%, complying with the empirical miscibility criterion. Thus, going back to Fig. 1, which relates the lattice constant with the F band peak energy ($E_F$), it allows us to propose another miscibility criterion, which will be denominated optical miscibility criterion (OMC) and will be based in the percentage variation of $E_F$. We estimate the maximum minus the minimum of the F band peak energies of the alkali halides that are used to form quaternary crystals. From this, it can be seen that quaternary crystals are a big crystallographic family represented in Fig. 4. This figure indicates that along the lines can be formed the binary crystals, over the triangles the ternary crystals and over the square the quaternary crystals. To find the molar fractions one must draw line segments from the points to the corners and consider that the magnitude of these segments should be 1. The information about composition does not appear in it, this would be important in a phase diagram. As the values of the EF for KCl, KBr, RbCl and RbBr are 2.313, 2.064, 2.05 and 1.87 eV respectively [3], the largest difference is between 2.313 and 1.87, *i.e.* between the F band peak energies of Kbr and RbBr respectively. Thus, the percentage change of the F band peak energy in the OMC is:

$$100(\text{EFmax} - \text{EFmin})/\ \text{EFmin} = 23.7$$

$$\text{and} \quad \text{OMC} = 23.7\% \qquad (2)$$

The maximum and minimum "energy peaks" give us the excess percentage between the two extreme quantities. It is considered that, using the four basic alkali halide components, would be possible to extract the ternaries that can be generated, suffice it that in the mixture a component of the basic components be omitted. So, four possible mixtures of three components or four possible ternaries can be obtained. The same logic is applied to a ternary basis, in which omitting one of the components allows to generate the known binary mixtures. This is schematized in Fig. 2.

The optical miscibility criterion would be that the maximum variation of the maximum absorption peak energy of the F band in the studied alkali halides is 23.7%, which will be a criterion alternative to the traditional one, under which the maximum variation of the lattice constant to have miscibility among alkali halides is 10 %. Even though this miscibility criterion was valid for this crystallographic family, the most reliable criterion for the entire set of alkali halides is of a lattice constant variation of 8 %, because for certain binary mixtures, this criterion does apply, while the other does not [11]. A similar thing can occur with the optical miscibility criterion, which is found with a variation of 23.7% of the maximum energy of the F band; for the entire set of alkali halides this percentage could be lower. In fact, returning to Fig. 1, we tried to design a mixture of 5 alkali halides, taking the 5 closest points observed, meaning, we considered a mixture of the salts KBr, RbCl, RbBr, KI and RbI. This mixture, which we will name quinary, was grown, and its first characterization was given by an Scanning Electron Microscopy (SEM); the images can be observed in Fig. 5. When the material was obtained, we observed that it was not transparent, which lead us to suppose that the crystal is not a single-phase crystal. The images in Fig. 2 show that it contains more than

TABLE II. Lattice constants obtained from difractometric results and the comparative values obtained calculating the values from Generalized Vegard's law, using data of Ref. 15.

| Mixed crystals | Lattice constants (Exp) | | Vegard's Generalized law |
|---|---|---|---|
| KCl0.33KBr0.33 RbCl0.33 | **6.4816** | **Ref[1]** | **6.367** |
| KCl0.50 KBr0.25 RbCl0.25 | **6.42** | Ref[[6] | **6.442** |
| KCl0.50KBr0.25 RbBr0.25 | **6.456** | **Ref[[7]** | **6.51** |
| KCl0.47 KBr0.39 RbBr0.14 * | **6.672** | Ref[12] | **6.516** |
| KCl0.25 KBr0.25 RbCl0.25 RbBr0.25 | **6.56** | Ref[8] | **6.67** |
| KCl0.30 KBr0.30 RbCl0.30 RbBr0.10 | **6.512** | Ref[[8] | **6.511** |

*Ternary phase of Quinary crystal. Ref. 12

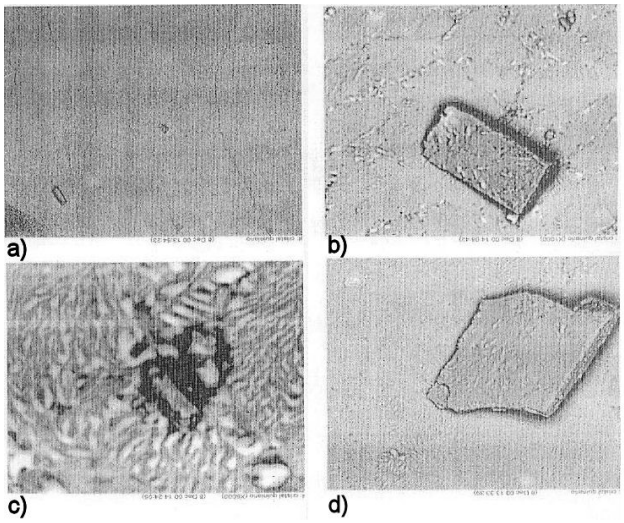


FIGURE 5. SEM images of the quinary material. The first shows a microcrystal; the second exhibits a close-up of the same microcrystal. In general, the images allow the supposition that the material has more than two phases.

two phases. A detailed study of the material by X-ray diffraction and high-resolution Transmission Electron Microscopy produced interesting results, that the quinary is formed by a pure phase of RbBr and two mixture phases: a ternary and a binary, with a coherent orientation of the three phases [12]. A recently study of a mixed crystal of two phases KCl:KBr:KI was performed by S. Perumal [13].

## 4. Conclusions

We have provided a panorama of some of the studies conducted on crystalline mixtures of alkali halides of more than two components, which before the work published in 1998 [1], were the only known ones. We found that there is a crystallographic family generated by a quaternary base that, at the same time, can be made into ternary crystals and, finally, these lead to the already known binary crystals. Obtaining these crystals opens up the possibility of obtaining materials with different physical parameters, such as the refraction index, dielectric constant, and Debye's temperature [14]. The most important contribution of this work has been to show that the key for obtaining another miscibility criterion is in Fig. 1, which links the lattice constant (horizontal axis) with the F band energy (vertical axis). This makes possible an alternative miscibility criterion than the one considered by the lattice constant - which is the most accepted criterion -, because in Fig. 1, one can see that the points closest to each other correspond to components that are miscible and, thus, consider the EF value (vertical axis) to determine a range of possible values that allow miscibility. This is why this criterion was called optical miscibility criterion, which is equivalent to the lattice parameter, but through the F band energy. We intended to provide an optical miscibility criterion based on the percentage variation of the F band energy and found that, for the crystallographic family, the maximum percentage variation in the involved crystals is 23.7%. Although the usual miscibility criterion based on the lattice constant works in most of the known cases, there are some exceptions. In the case of the optical miscibility proposed herein, more research is needed to know just how general it can be and what possible exceptions might fail. An optical miscibility criterion that all the binaries would follow is that the $E_F$ difference should not exceed 20% would be a more general criterion.

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