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The influence of ions' substitution on the optical properties of A_2MX_4 crystals

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Abstract In this article, results based on the research of optical properties of A_2MX_4 type crystals (A—organic cation, M—metal, X—halogen) composed of different chemical elements are presented. These crystals were grown by the evaporation method from water solutions of AX and MX_2 compounds in an appropriate molar ratio. The conducted X-ray investigations show a different crystal structures, ranging from tetragonal to triclinic ones. Also, the structure of the ion complex for Cu^{2+} crystals varied. The investigation showed both $CuCl_4^{2-}$ tetrahedral and $CuCl_4 \cdot 2H_2O^{2-}$ octahedral deformed complexes in investigated crystals. Additionally, the optical spectra of the samples were measured in the range of 250–850 nm. Based on the crystal field theory, it was shown that the shape of absorption spectra and colour of the crystals depend on the distortion of these complexes.

Introduction

Over the past few decades ferroelectric crystals of the A_2MX_4 type, also known as A_2BX_4 in literature worldwide, have had a great deal of interest and attention [1, 2]. In the above formula, A is the alkali-metal ion (K^+, Rb^+, Cs^+), the ammonium group NH_4^+or the organic cation $NH_n(C_mH_{2m+1})_{4-n}$ (n = 0...3); M—the transition metal ion (most frequently Mn^{2+}, Co^{2+}, Cu^{2+}) or the zinc group (Zn^{2+}, Cd^{2+}, Hg^{2+}), whereas X is the halogen ion (Cl^-, Br^-, F^-) or the oxygen ion. The first investigated crystals were the best-known K_2SeO_4 [3, 4] and $[NH_4]_2BeF_4$ [5] crystals. The majority of known crystals of the A_2MX_4 type display a structure and properties similar to the K_2SeO_4 crystals. There is abundant literature on the structure and properties of crystals with non-organic cations (e.g. Rb_2ZnCl_4, Rb_2ZnBr_4, K_2ZnCl_4, K_2ZnBr_4) [6–9]. A lot of attention was also given to the crystals with organic cations, especially tetramethyloammonium ones (TMA^+—$N(CH_3)_4^+$) [10–12]. There were also examined doped crystals such as $K_{2-x}Rb_xZnCl_4$ [13] or $[NH_2(C_2H_5)_2]_2Cu_xZn_{1-x}Cl_4$ [14]. At high temperatures (>300 K), these crystals are mostly paraelectric and have a orthorhombic structure of the D_{2h}^{16} (Pnma) space group. At lower temperatures, the crystals can be ferroelectric and usually belong to the C_{2v}^{9} (Pna2) or C_{2h}^{5} (P2′/c) group.

There are many reasons for the continuing interest in the A_2MX_4 type crystals. The structural and calorimetric investigations of the crystals showed existence of a large number of phases and phase transitions, including the occurrence of paraelectric, ferroelectric and ferroelastic phases with the simultaneous existence of the structure modulation [15]. Particular attention was paid to the existence of the incommensurate modulation of the structure, known as the IC phase [2, 15–17].

A term of modulated structure can be used for materials with an optional periodic or semiperiodic disorder of crystals structure with a period distinctly greater than dimension of an elementary cell. In the case of A_2MX_4 crystals the translate modulation with period 1/2, 1/3, 1/4 or 2/5 was mainly observed [2]. Materials with incommensurate modulated structures have no translation symmetry, although save the typical features of the crystals: anisotropy, stiffness, hardness, etc. This phenomenon and its influence on the optical properties of birefringence

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have been discussed in the author's previous works [18, 19].

Another characteristic feature of these crystals is the occurrence of the ferroelectric phase which is observed within a certain temperature range, depending on the chemical composition of a given crystal [20].

Another set of qualities characterising these crystals are their optical properties, either in terms of the refractive index or the optical absorption coefficient [1]. The optical absorption of light in a particular light wavelength range influences the colour of the grown crystals. The spectral properties of material containing transition metal ions are known to be formed by the electron configuration of the *d* subshell of such metal ions.

The additional factor influencing the optical properties of these crystals is the crystal field splitting of the basic terms of the free ion. This phenomenon will be especially important to explain the optical properties of the A_2CuX_4 crystals, because the free Cu^{2+} ion contains only one term (^2D). Only the interaction of the ligands (halogens and water), splitting of this term, leads to observable energy transitions within the spectrum's visible range. Obviously, the splitting of terms induced by the crystal field can also have an influence on the optical properties of crystals containing other metal ions.

Precise analysis of optical spectra of crystals with metal ion complex typically requires calculating wave functions of molecular orbitals and their corresponding energies. Unfortunately, the calculations are usually complicated. However, in many cases, the much simpler crystal field theory [21] may be useful for analysing the influence of complex distortion of energy states in central metal ion. It is of crucial importance, as in real A_2MX_4 crystals, that such complexes usually assume different forms. In literature on A_2MX_4 crystals there is a shortfall of precise analysis of such phenomena.

The aim of the article is to analyse the influence of the ion substitution on the optical properties of crystals belonging to the broad A_2MX_4 group. This analysis is mainly based on experimental research, including crystal growth, structural investigations and spectral measurements.

Crystal growth

The A_2MX_4 type crystals, investigated by the author, were grown from aqueous solutions of compounds AX and MX_2 at a stoichiometric ratio of 2:1 (0.2 mole of AX compound and 0.1 mole of MX_2 compound). Both compounds were dissolved in distilled water. The author attempted to achieve the saturation point by allowing the growing to shorten time of the crystals. The solution was filtered through filter paper and was left to evaporate at a constant temperature of 25 °C. The growing time varied from 2 to 6 months. In this way the following crystals were grown: K_2ZnCl_4 (K-ZnCl), K_2MnCl_4 (K-MnCl), K_2CuCl_4 (K-CuCl), $[NH_4]_2CuCl_4$ (A-CuCl), $[N(CH_3)]_2CuCl_4$ (TMA-CuCl), $[NH(CH_3)_3]_2CuCl_4$ (TrMA-CuCl), $[N(CH_3)_4]_2ZnCl_4$ (TMA-ZnCl), $[N(C_2H_5)_4]_2CuCl_4$ (TEA-CuCl), $[N(C_2H_5)_4]_2CuCl_2Br_2$ (TEA-CuClBr), $[N(C_3H_7)_4]_2ZnCl_2Br_2$ (TPA-ZnClBr), $[N(C_3H_7)_4]_2CuCl_2Br_2$ (TPA-CuClBr), $[N(C_3H_7)_4]_2CoCl_2Br_2$ (TPA-CoClBr) and $[N(C_3H_7)_4]_2CuBr_4$ (TPA-CuBr). The last four crystals were grown for the first time.

The samples were ground and polished with diamond polish paste in order to obtain the plates of equal thickness of around 1 mm. The colour of the crystals varied and was mainly dependent on the metal ion. As expected, the crystals with Zn^{2+} ion were transparent (colourless). The K-MnCl crystal was pale pink, resembling the solution in which it was grown. The TPA-CoClBr crystal was dark blue, even though the solution in which it had grown was dark pink. This difference demonstrates the influence of the crystal field on the optical properties of the crystal. The crystals with Cu^{2+} ion had different colours: blue (K-CuCl, A-CuCl), green (TrMA-CuCl), yellow (TMA-CuCl), amber (orange) (TEA-CuCl) or they were opaque (for X = Br). Such a clear variation of colour is characteristic of only Cu^{2+} ion crystals, and that is why this particular type of crystal was chosen for further investigation.

Crystal field interaction

According to the crystal field theory, the *3d* orbitals of transition metal ions interact electrostatically with the point charges of ligands surrounding them. The distribution of charges for particular orbitals of the central metal ion can be mapped out simply on the basis of their wave function. In the simplest case, it can be assumed that the wave functions have an identical form to that of the appropriate functions of the hydrogen-like ion. Their form in the polar coordinates is as follows [22]:

$$\begin{aligned}
3d_{z^2} &= \frac{1}{\sqrt{6}}\Gamma\rho^2 e^{\frac{-\rho}{3}}\left(3\cos^2\theta - 1\right)\\
3d_{xz} &= \sqrt{2}\Gamma\rho^2 e^{\frac{-\rho}{3}}\sin\theta\cos\theta\cos\varphi\\
3d_{yz} &= \sqrt{2}\Gamma\rho^2 e^{\frac{-\rho}{3}}\sin\theta\cos\theta\sin\varphi\\
3d_{x^2-y^2} &= \frac{1}{\sqrt{2}}\Gamma\rho^2 e^{\frac{-\rho}{3}}\sin^2\theta\cos 2\varphi\\
3d_{xy} &= \frac{1}{\sqrt{2}}\Gamma\rho^2 e^{\frac{-\rho}{3}}\sin^2\theta\sin 2\varphi
\end{aligned} \tag{1}$$

where $\Gamma = (1/(81\sqrt{\pi}))(Z/a_0)^{\frac{3}{2}}$, $\rho = Z_r/a_0$—modified radial variable $a_0 = \varepsilon_0 h^2/\pi\mu e^2 \approx 0{,}0529$ nm—radius of the first orbital of hydrogen.

The Z parameter for the hydrogen-like ion denotes the atom charge. In this case, it defines the extent of the electron clouds for particular orbitals. The concentration of the cloud around the nucleus of the central ion grows with the increasing value of this parameter.

In order to estimate the energy of the ligand's interaction for a given *3d* orbital, it is necessary to calculate the integration in the spherical coordinates system with a variable charge density, which is proportional to the complex squared appropriate wave function. The total energy of interaction of all the ligands surrounding the metal ion is obviously the sum of interactions of every ligand taken separately, and can be calculated as follows:

$$E_{d_\alpha} = \sum_i \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \frac{k \cdot e^2 \cdot [d_\alpha(\vec{r})]^2 \cdot r^2 \sin(\theta) dr d\theta d\varphi}{|\vec{R}_i - \vec{r}|} \tag{2}$$

where d_α is the function describing the given orbital, whereas $\vec{R}_i$ determines the positions of ligands.

The above relationship makes it possible to calculate the splitting energy of the crystal field of any molecule. For configurations d^1 or d^9 (Cu^{2+} ion), the difference of interaction energy is equal to the splitting energy of particular terms. Integral calculations (2) were carried out with the MathCad 2000 program. However, even by knowing the actual position of the ligands, it is impossible to calculate the actual energy value due to the lack of a precise parameter Z value. Therefore, such considerations are exclusively comparative in character.

Experimental setup

The grown crystals were investigated by the X-ray study and measurement of optical spectra. The X-ray investigations were carried out using four-circle diffractometer (Oxford Diffraction) at room temperature. Structure solution and refinement were carried out using the SHELXS-97 program package. The measurements of the optical spectra were taken in unpolarised light with a AVS-S2000 (Oceanoptics) spectrometer in range of 250–850 nm. The Mini-D2 deuter-halogen lamp was used as the source of light.

Results and discussion

The optical spectra of crystals with Zn^{2+}, Mn^{2+} and Co^{2+} ions

As was mentioned above, all crystals with Zn^{2+} are colourless and similar to the solution in which they were grown. The well-known K-ZnCl crystal and the newly created TPA-ZnClBr crystal were chosen for investigations. The samples were ground and polished to obtain thin plates of around 1 mm thickness. The results of the measurements are presented in Fig. 1.

It can be seen that these crystal are transparent in the visible range of the spectrum. The Zn^{2+} ion contains only one term ^1S, which is not split in the crystal field. For this reason no electron transitions within the ion are possible for the energy in the measured range. However, the transition to configuration $3d^94s^1$ is possible in the ultraviolet energy range [23]. The decrease in optical transmittance for shorter waves is probably caused by the light diffusion in non-homogenous crystals. The absorption margin for the investigated crystals corresponds to waves below 250 nm, which is typical of other crystals from the A_2ZnX_4 group. The infrared spectral investigations showed that the TPA-ZnClBr crystal is transparent up to around 2250 nm, whereas for around 1180, 1370 and 1510 nm, absorptions bands were observed, which was probably due to impurities [24].

In the absorption spectrum of the K-MnCl crystal a number of small maxima are observed which may be connected with internal transitions in the Mn^{2+} ion (Fig. 2).

These maxima are mainly observed for short waves which account for the light pink colour of the crystal. The Mn^{2+} ion has only five electrons in the *3d* subshell, yet the number of possible terms for the free ion in this configuration is quite high. The basic term in Mn^{2+} is the non-degenerate ^6S term, which means that every orbital has only one electron. This term is not split in the crystal field, so only transitions to higher excited terms with smaller multiplicity can be taken into consideration. However, transitions of this type are impossible because of spin. That is why only weak absorption bands are observed in this crystal for short waves, which is probably related to

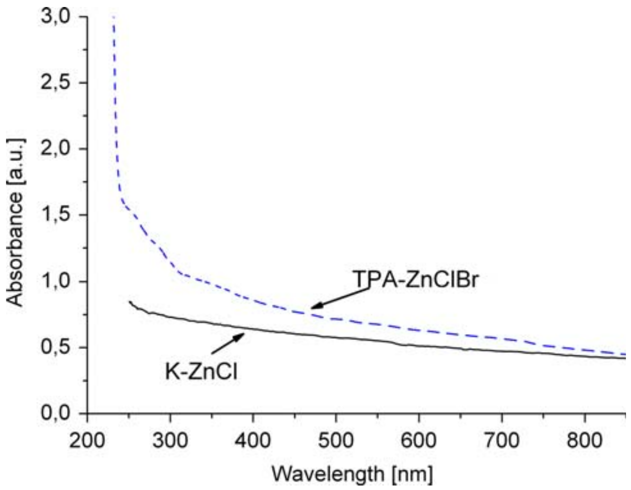

Fig. 1 Absorption spectra of K-ZnCl and TPA-ZnClBr crystals

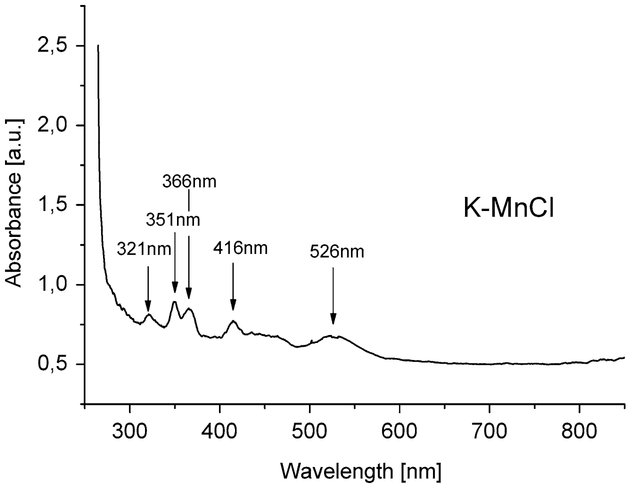

Fig. 2 Absorption spectrum of the K-MnCl crystal

transitions between the ^{6}S term and terms that have arisen as a result of splitting of tetraplet terms (^{4}G, ^{4}F) in the crystal field. The fact that the colour of the crystal is similar to the colour of the solution proves that the influence of the crystal field on its optical properties is negligible.

The TPA-CoClBr crystal, which was grown for the first time by the author is blue, though the solution was pink. This indicates that the crystal field has a much greater impact on the optical properties than in the case of the former crystal. Figure 3 shows the absorption spectrum of the crystal and its aqueous solution. This crystal is transparent in the 310–600 nm band and above 760 nm, whereas for the wavelength of 600–760 nm, strong optical absorption is observed, which makes the crystal opaque in this band.

For the water solution itself, such a strong absorption within the investigated range did not occur, which accounts for the differences in the colours of the crystal and solution. This crystal has the absorption spectrum clearly similar to the TMA_2CoCl_4 crystal described in literature [1] (see Fig. 4).

The Co^{2+} ion has the $3d^7$ configuration, in which the basic term is the ^{4}F term. The transition to the nearest excited ^{4}P term is less probable due to the Laporte orbital rule [22]. The main observed absorption bands correspond to transitions between the energy levels arising as a result of splitting of the basic term in the presence of ligands. Both crystals display strong absorption in the 600–800 nm range, linked with the transition from the fully symmetrical $A_1(^4F)$ basic term to the $T_2(^4F)$ term. Other stronger absorptions correspond to the transitions of $T_1(^4F)$ and $T_1(^4P)$ terms. The wavelengths corresponding to these transitions for both crystals are approximately the same. This case, therefore, shows that the substitution of either the X^- or A^+ ion does not have a significant influence on the optical properties of crystals with Co^{2+} ion.

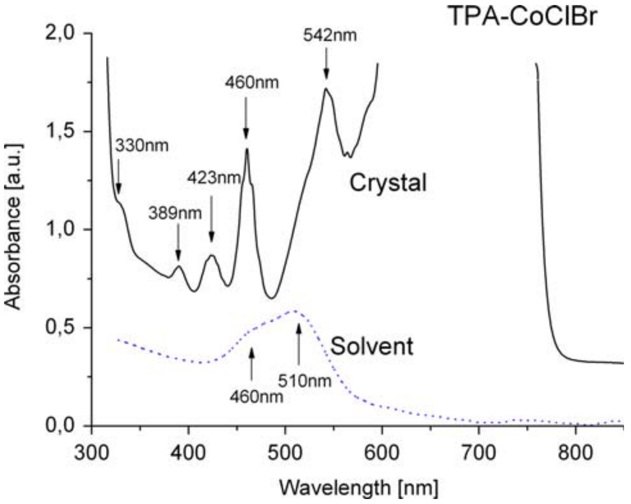

Fig. 3 Absorption spectrum for the TPA-CoClBr (*continuous line*) and its aqueous solution (*broken line*)

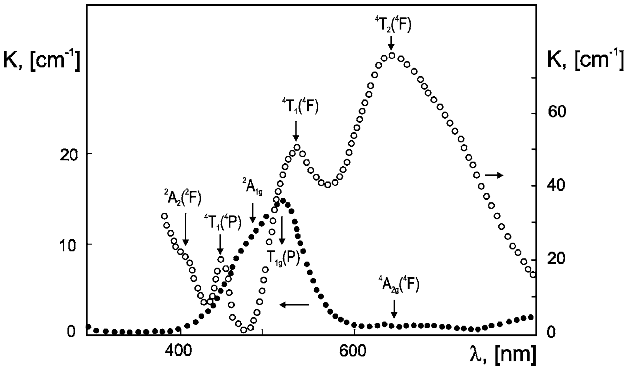

Fig. 4 Absorption spectrum for the TMA_2CoCl_4 (o) crystal and its water solution (•) [1]

The spectra of the aqueous solutions of both compounds have similar form. The solutions have observable absorption bands of wavelengths of around 430 and 510 nm. The observed absorption bands have higher energy in the case of solutions, probably due to setting of the cobalt ions in an octahedral environment in the aqueous solution. In the crystal they are set in a tetrahedral environment, which is further supported by the weaker optical absorption in the solution due to a higher symmetry of octahedral complexes [1].

The optical spectra of crystals with Cu^{2+} ion

The crystals with copper ions are particularly interesting because of the diversity of their structure and optical properties. These crystals appear in different colours, depending on the type of A^+ cation and the halogen ion. The crystals with Br^- ions are practically non-transparent

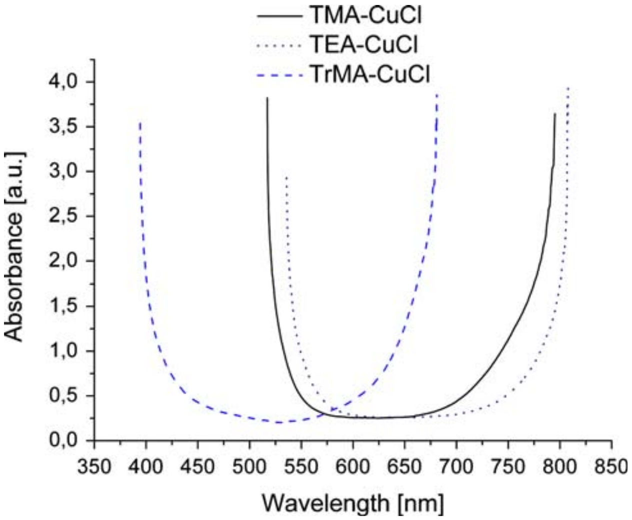

Fig. 5 The absorption spectra of A-CuCl (A = TMA$^+$, TEA$^+$, TrMA$^+$) crystals

and were not examined spectroscopically within the visible range. The infrared investigation of the TPA-CuClBr crystal showed that the absorption edge is about 1800 nm [24]. The differences in the optical properties of Cu^{2+} crystals between bromine and chlorine ions can be explained on the basis of the ligand-to-metal charge transfer (LMCT) [25]. The spectral investigations were carried out for chlorine crystals.

The Cu^{2+} ions have one basic ^{2}D term. In the crystal field this term can be split into a maximum of five energy levels, the values of which strongly depend on the shape and symmetry of the molecule. The transitions between these levels are responsible for the shape of the optical spectra. In these spectra, two strong absorption bands can be distinguished, limiting the transparency of the crystals for the short and long wavelengths.

The absorption spectra for some crystals of A-CuCl type are presented in Fig. 5.

The differences in the position of the absorption bands for each crystal can be explained by the differences in their molecular structure. The structural investigation was performed on the TMA-CuCl, TEA-CuCl and TrMA-CuCl crystals.

At room temperature, the TMA-CuCl crystal has a symmetry typical of the A_2MX_4 crystals. The X-ray investigation of the grown sample showed that it has orthorhombic structure and belongs to the D_{2h}^{16} space group. The structure of this crystal is characteristic of the high-temperature phases of the A_2MX_4 crystals. The lattice constants were fixed at a = 12.17 Å, b = 9.1 Å, c = 15.25 Å. The constant ratio c/b is approximately equal to $\sqrt{3}$, and for this reason, similarly to other crystals (e.g. Rb_2ZnBr_4 [26] or $[N(CH_3)_4]_2MnCl_4$ [27]) the structure can be termed pseudo-hexagonal. The TEA-CuCl crystal has a distinctly different structure (tetragonal—P4/n) but the structure of the $CuCl_4^{2-}$ complex is quite similar in both crystals. The crystal data are presented in Table 1.

The $CuCl_4^{2-}$ complexes form a clearly oblate tetrahedron. Two perpendicular symmetry planes, created by the triplet Cl_1–Cu–Cl_2 and Cl_3–Cu–Cl_4 ions, can be distinguished here. The intersecting edge of these planes is simultaneously the double axis of symmetry. The symmetry of the $CuCl_4^{2-}$ complex can therefore be treated as that belonging to the D_{2d} group.

Table 1 Crystal data for the TMA-CuCl and TEA-CuCl crystals

	TMA-CuCl	TEA-CuCl
Formula	$C_8H_{24}Cl_4CuN_2$	$C_{16}H_{40}$ Cl_4CuN_2
Space group	Pnma (D_{2h}^{16}) orthorombic	P4/n (C_{4h}^{3}) tetragonal
Cell parameters	a = 12.17 Å, b = 9.10 Å, c = 15.25 Å, V = 1689.62 Å^3	a = b = 14.03 Å, c = 12.48 Å, V = 2455.75 Å^3
Bonds	Bond lengths (Å)	
Cu_1–Cl_1	2.23	2.22
Cu_1–Cl_2	2.23	2.22
Cu_1–Cl_3	2.235	2.28
Cu_1–Cl_4	2.245	2.28
Cu_1–N_1	4.86	5.01
Cu_1–N_2	4.89	5.01
N_1–C_{11}	1.46	1.5
	Angle (°)	
Cl_1–Cu_1–Cl_2	126.3	126.2
Cl_1–Cu_1–Cl_3	101.6	102.9
Cl_3–Cu_1–Cl_4	131.3	128.1
Cl_2–Cu–Cl_4	99.9	98.9

The organic groups surrounding this complex lie in close proximity to the planes selected by various triplets of Cl_i–Cu–Cl_j ions. The structural investigations have also revealed that the hydrogen ions in the organic groups create hydrogen bonds with halogens in the $CuCl_4$ complex. The Cu–Cl distances are nearly identical and are 2.23–2.24 Å approximately. The organic groups are found at a significantly greater distance, above 4.8 Å.

On the basis of actual interatomic distances and the model presented above, the interaction energy of ligands of particular orbitals was calculated for both crystals. Since the crystal field's interaction diminishes quickly with an increasing distance ($\sim r^{-5}$), the calculations took into account only the interaction of the four nearest chlorine ions. The obtained values were compared with the splitting energies of the ideal tetrahedral field, in which the distances Cu–Cl are the same as in the real molecule of the examined crystal, i.e. about 2.235 Å.

A detailed account of the energy distribution in particular terms is presented in Fig. 6.

Their names are based on character tables representing specific symmetry groups [28]. The initial splitting of energy in an ideal tetrahedral field (T_d symmetry) is denoted as $\Delta_{t.}$ In the real molecule, the terms are clearly split. The most energy-efficient is the A_1 term, because the smallest electrostatic interaction relates to orbital d_{z^2} .The interaction on d_{xz} and d_{yz} orbitals is almost identical, which results from the fact that the symmetry of the complex is close to D_{2d}. They form a degenerated E term. Excitation of the electron of the base term to E term requires energy of the order of $1.77\Delta_t$ energy. Transition to A_1 term (d_{z^2} orbital) requires energy equal to $2.64\Delta_t$. The energy of this transition is comparable to the splitting energy in the octahedral field.

To complement the spectra analyses, the transition probability resulting from the group theory should be observed. Based upon the group theory and the character tables for the D_{2d} symmetry, it is easy to show that transition from term B_2 to B_1 is impossible. Therefore, transitions from B_1 (xy) to A_1 (z^2), should correspond to the observed absorption band for short waves, whereas long wave absorption band may be connected with transitions from B_1 (xy) to E term.

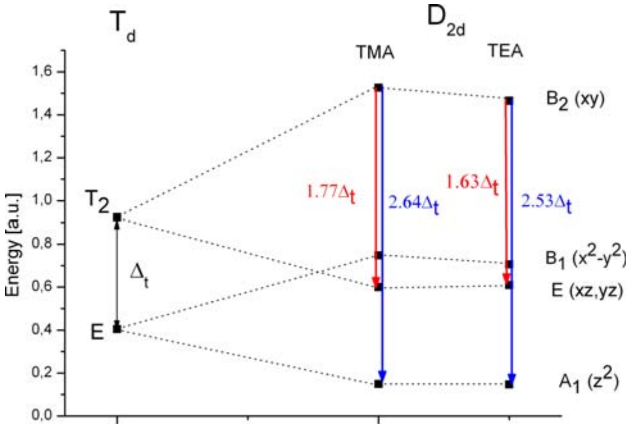

Fig. 6 Calculated distribution energy of terms for the TMA-CuCl and TEA-CuCl crystals

The TrMA-CuCl crystal has a clearly different structure. Despite maintaining the stoichiometry during the growth process, the crystal is characterised by the $[NH(CH_3)]CuCl_3 \cdot 2H_2O$ formula. The crystal data are presented in Table 2.

This crystals structure is monoclinic with C_{2h}^5 space group. The angle between the a and b axes equals to approximately 91.89°. This group is also characteristic of some of the A_2CuCl_4 crystals, e.g. $[NH_3C_2H_5]_2CuCl_4$ [29]. The lattice constants were fixed at $a = 7.5$ Å, $b = 7.89$ Å, $c = 16.76$ Å. In this crystal alternate layers of $CuCl_2$ chains and layers of the $TrMA^+$ organic groups and chlorine ions are observed. The copper ions lie in the middle of a parallelogram with four chlorine ions at the corners. Neighbouring parallelograms lie on different plates. Additionally, the metal ions are adjoined to two water molecules, located perpendicularly to the plane determined by the parallelogram. At a further distance, there lies the next chlorine ion and the organic group. The shape and dimensions of the first and third $MX_4 \cdot 2H_2O$ complex are identical and different from the middle complex. The short Cu–Cl distances are 2.31 Å (2.27 Å), whereas the long ones are 2.75 Å (2.90 Å) respectively.

The halogen ions and the water molecules (dipoles) create a strongly degenerated octahedral environment for

Table 2 Crystal data for the TrMA-CuCl crystal

Formula	$C_3H_{14}Cl_3CuN_2O_2$
Space group	$P2'/c$ (C_{2h}^5) monoclinic
Cell parameters	$a = 7.5$ Å, $b = 7.89$ Å, $c = 16.76$ Å $\beta = 91{,}88°$, $V = 990.74$ Å^3
Bonds	Bond length (Å)
$Cu–Cl_1$	2.31 (2.27)
$Cu–Cl_2$	2.75 (2.90)
$Cu_1–Cl_3$	4.57
$Cu_2–Cl_3$	4.56
Cu–O	2.01 (1.97)
Cu–H (H_2O)	2.41
Cu_1–N	4.25
Cu_2–N	4.37
N–C	1.48
	Angle (°)
$Cl_1–Cu–Cl_2$	93.5 (96.6)
$Cl_2–Cu–Cl_1$	86.5 (83.4)
Cl–Cu–O	90.6

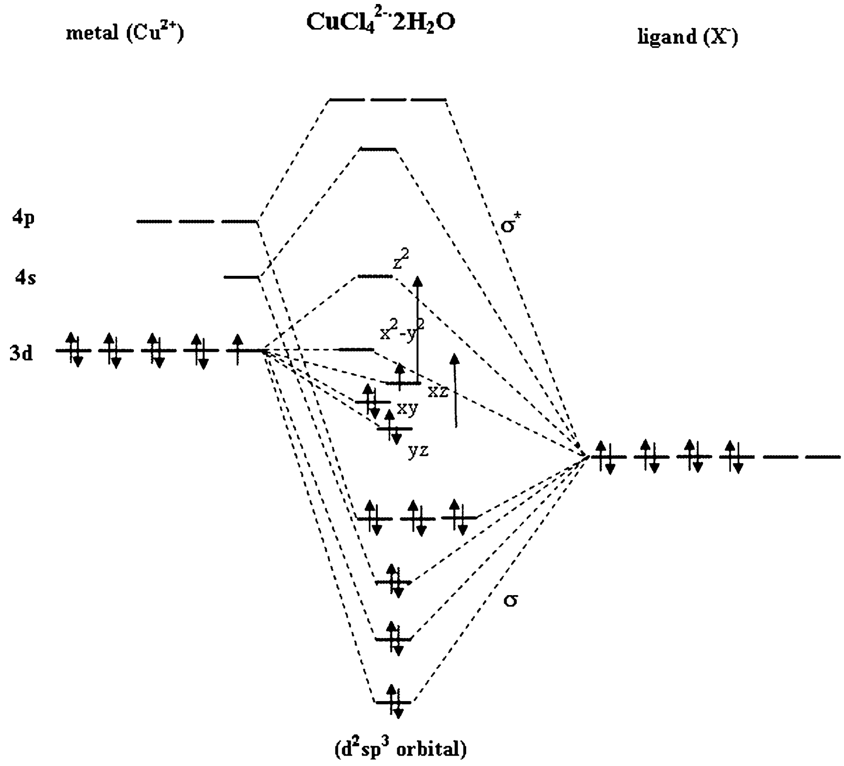

Fig. 7 Electron states for $CuCl_4 \cdot 2H_2O$ octahedral complex in the TrMA-CuCl crystal

the Cu^{2+} ion. In the $MX_4 \cdot 2H_2O$ complex, the symmetry centre (copper ion) and one plane, containing four halogen ions, and the axis of symmetry, passing through both water molecules and copper ion, can be distinguished. Therefore, the complex symmetry belongs to the C_{2h} group. The analysis of the selection rules for the C_{2h} symmetry group, based on the table of characters, revealed that no transitions are possible because all orbitals are symmetrical (*g*-type).

Appearance of absorption bands in TrMA-CuCl crystals should be considered upon by a slightly different mechanism. It is known that in octahedral complexes, a d^2sp^3 hybrid orbitals are formed. In such a case, two orbitals from *3d* subshell ($x^2 - y^2$ and z^2) form molecular orbitals with *p*-orbitals of halogen ion. Thus, to explain the shape of spectrum, it is necessary to resort to the Molecular Orbit Theory [21].

Electron states for $CuCl_4 \cdot 2H_2O$ octahedral complex are presented in Fig. 7.

In this case, absorption bands for short and long waves are connected with transition from *d* orbitals (*xy*, *xz*, *yz*) to antibonding molecular orbital (z^2) and antibonding molecular orbital ($x^2 - y^2$), respectively.

Conclusions

This work presents the main results of the research on the spectral properties of the A_2MX_4 type crystals of diverse chemical composition. The optical properties of these crystals are dependent on the electron configuration of metal ions, and also on the crystal field associated with the crystal's molecular structure. It has been shown that the substitution of the A^+ cation can bring about the deformation of $CuCl_4$ polyhedrons, which results in clear diversification of energy levels in the Cu^{2+} ion. Furthermore, if the deformation of the molecule undergoes change under the influence of temperature, the thermochromic effect should be visible. The spectral investigations of the crystals with the Cu^{2+} ion showed that the optical spectra can clearly vary at different temperatures. The result of this, for example, is the thermochromic effect observed in the $[NH_4]_2CuCl_4$ crystal [30]. This effect can have a practical application in wireless temperature sensors, discussed by the author in paper [31].

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