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The Influence of Deviations from 1:1 Order in Perovskites on Optical Properties

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Vibrational and electronic spectra of compositions $Ba_2Mg_{1-x}Li_{0.8x}W_{1+0.2x}O_6$ and $Sr_{1+x}La_{1-x}Li_{1-0.2x}$-$W_{1+0.2x}O_6$ are reported. The vibrational spectra show the presence of clusters of WO_6^{6-} octahedra. Large clusters quench the luminescence that has been found for the compositions with $x = 0$.

1. Introduction

In our laboratory, research has been performed on vibrational and electronic spectra of ordered perovskites with the general formula A_2BWO_6 (*1*, *2*). In these compounds, the WO_6 octahedra do not have oxygen ions in common; thus, they can be considered as isolated molecular groups. It seemed interesting to study the influence of a deviation from 1:1 order in these compounds. Such a deviation would result in the presence of corner-sharing WO_6 octahedra, which may show optical properties that are different from those of the isolated octahedron. It has been suggested (*2*) that in Ba_2MgWO_6 there is a slight deviation from perfect 1:1 order, resulting in WO_6 clusters with a luminescent emission that differs considerably from the isolated octahedron (yellow emission color instead of blue). It is further interesting to note that in the structurally related series Ba_2MgWO_6–$BaNa_{0.4}W_{0.6}O_3$–WO_3 the absorption edge shifts to longer wavelengths and that the tungstate luminescence disappears.

Here we report on the system $Sr_{1+x}La_{1-x}$-$Li_{1-0.2x}W_{1+0.2x}O_6$ ($SrLaLiWO_6$ (*3*), in which $Li^+ + 5La^{3+}$ are replaced by $5Sr^{2+} + W^{6+}$) and $Ba_2Mg_{1-x}Li_{0.8x}W_{1+0.2x}O_6$ (Ba_2MgWO_6, in which $5Mg^{2+}$ are replaced by $4Li^+ + W^{6+}$). These systems offer the possibility of creating a limited deviation from the 1:1 stoichiometry on the smaller-cation sites in such a way that oxygen-sharing tungstate octahedra occur.

2. Experimental

Samples were prepared by the usual techniques. They were analyzed by X-ray diffraction (Cu$K\alpha$ radiation, Philips diffractometer). Samples showed the X-ray diagram of 1:1 ordered perovskites for $0 \leqq x \leqq 1$ in the system $Sr_{1+x}La_{1-x}La_{1-0.2x}W_{1+0.2x}O_6$ and for $0 \leqq x \leqq 0.3$ in the system $Ba_2Mg_{1-x}Li_{0.8x}$-$W_{1+0.2x}$-O_6.

The performance of the optical measurements has been described previously (*4*). The Raman measurements were carried out at the Analytical Laboratory of this University (by Dr. J. H. van der Maas).

3. Results and Discussion

3.1. Vibrational Spectra

The vibrational spectra of Ba_2MgWO_6 and $SrLaLiWO_6$ have been described in previous papers (*1*, *5*). Frequencies and assignments of the observed bands in the systems under discussion are presented in Tables I and II. We notice that with increasing disorder, the bands in the vibrational spectra become broader and that the T_{1u} modes (ν_3 and ν_4) appear in the Raman spectrum. This indicates a deviation from perfect 1:1 order and the disappearance

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TABLE I

FREQUENCIES AND ASSIGNMENTS OF THE BANDS IN THE VIBRATIONAL SPECTRA OF $Sr_{1+x}La_{1-x}Li_{1-0.2x}W_{1+0.2x}O_6$

	$x=0$		$x=0.125$		$x=0.250$		$x=0.500$	
	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared
$A_{1g}(\nu_1)$							860 (sh)	
			840 (sh)[a]		840 (sh)		840	840
	815	805	815	805	815	805	815 (sh)	
$T_{1u}(\nu_3)$		620		630	640 (vw)	640	650 (w)	650
$T_{2g}(\nu_5)$	460		460		460		460	
$T_{1u}(\nu_4)$		360		360		360	365	360

[a] vw = very weak; w = weak; sh = shoulder; all values in cm^{-1}.

TABLE II

FREQUENCIES AND ASSIGNMENTS OF THE BANDS IN THE VIBRATIONAL SPECTRA OF $Ba_2Mg_{1-x}Li_{0.8x}W_{1+0.2x}O_6$

	$x=0$		$x=0.1$		$x=0.3$	
	Raman	Infrared	Raman	Infrared	Raman	Infrared
$A_{1g}(\nu_1)$					850 (sh)[a]	
	815		810		810	
			770 (sh)		770 (sh)	
$T_{1u}(\nu_3)$		605	595 (vw)	605	595 (w)	605 (sh)
		640 (sh)		640 (sh)		640
$T_{2g}(\nu_5)$					470	
	445		445		445	
			435 (sh)		435 (sh)	
$T_{1u}(\nu_4)$		370		370	370	370

[a] vw = very weak; w = weak; sh = shoulder; all values in cm^{-1}.

of inversion symmetry at the site of part of the W^{6+} ions, respectively. This is not unexpected. In tungstates A_2BWO_6 with 1:1 ordered perovskite structure, each WO_6^{6-} octahedron shares corners with six BO_6 octahedra. The B sites are occupied by Li^+ in $SrLaLiWO_6$ and by Mg^{2+} in Ba_2MgWO_6. When disorder occurs on the B-sublattice the surrounding BO_6 octahedra are no longer identical for all WO_6^{6-} groups. The vibrational spectra confirm, therefore, the presence of different types of WO_6^{6-} octahedra.

Especially the Raman-active A_{1g} mode (ν_1) which is very sensitive to ordering phenomena (*6*) clearly shows a number of subbands. In the Raman spectra of the system $Sr_{1+x}La_{1-x}Li_{1-0.2x}W_{1+0.2x}O_6$ we observed in addition to the single 815 cm^{-1} peak of $SrLaLiWO_6$, two subbands in the region of the A_{1g} mode: one at 840 cm^{-1} and another at 860 cm^{-1}. In $Sr_{1.5}La_{0.5}Li_{0.9}W_{1.1}O_6$ the 840 cm^{-1} peak has even higher intensity than the peak at 815 cm^{-1}. It seems reasonable to assume that, roughly speaking, the band at 840 cm^{-1} is due to a

WO_6^{6-} octahedron surrounded by five Li neighbors and one W neighbor and that the 860 cm^{-1} peak is due to a WO_6^{6-} octahedron sharing corners with two or more WO_6^{6-} octahedra.

In the system $Ba_2Mg_{1-x}Li_{0.8x}W_{1+0.2x}O_6$, we have also found two subbands in the ν_1 region, one at lower (770 cm^{-1}) and another at higher (850 cm^{-1}) energy than the single ν_1 peak of Ba_2MgWO_6 (815 cm^{-1}). The results for the system $Sr_{1+x}La_{1-x}Li_{1-0.2x}W_{1+0.2x}O_6$ suggest that the ν_1 frequency shifts to higher energy if the number of W–O–W contacts increases. This is also not unexpected from other results (*7*, *8*). Therefore, we are inclined to assign the 770 cm^{-1} peak to a WO_6^{6-} octahedron with five Mg neighbors and one Li neighbor and the 850 cm^{-1} peak to a WO_6^{6-} octahedron surrounded by five Mg neighbors and one W neighbor.

3.2. Luminescent Properties

In the system $Sr_{1+x}La_{1-x}Li_{0.8x}W_{1+0.2x}O_6$, the emission and excitation bands of $SrLaLiWO_6$ and $Sr_{1.25}La_{0.075}Li_{0.95}W_{1.05}O_6$ are identical. At 5°K, we observed a blue emission peaking at 2.55 eV. The excitation spectrum at this emission shows maximal intensity at 4.20 ev (*9*). In general, the luminescence becomes less efficient with increasing value of x without clear changes in the spectra. From the diffuse reflection apectra we learn that the absorption edge is at longer wavelength for higher values of x. With increasing value of x, the absorption edge becomes less steep.

The luminescence of Ba_2MgWO_6 has been described earlier (*1*, *2*). Figure 1 shows the emission spectra of Ba_2MgWO_6 and $Ba_2Mg_{0.9}Li_{0.08}W_{1.02}O_6$ at 5°K. Under 4.50 eV excitation, the low-energy emission in $Ba_2Mg_{0.9}Li_{0.08}W_{1.02}O_6$ is relatively stronger than the analogous long-wavelength emission of Ba_2MgWO_6. In the system $Ba_2Mg_{1-x}Li_{0.8x}W_{1+0.2x}O_6$ the luminescence becomes also less efficient for higher values of x. Figure 2 gives the excitation spectra of the low-energy emission for the various compositions at room temperature. In these spectra, we observed an additional low-energy excitation band for $Ba_2Mg_{0.9}Li_{0.08}W_{1.02}O_6$ and $Ba_2Mg_{0.7}Li_{0.24}W_{1.06}O_6$.

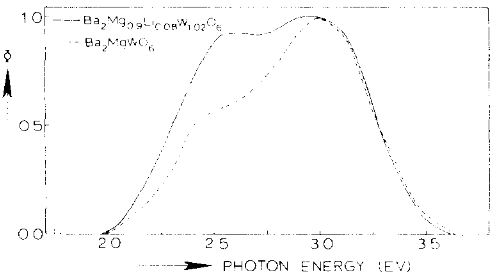

FIG. 1. Spectral energy distribution of the emission of Ba_2MgWO_6 and $Ba_2Mg_{0.9}Li_{0.08}W_{1.02}O_6$ at 5°K. Exciting photon energy: 4.50 eV. Φ gives the radiant power per energy interval in arbitrary units.

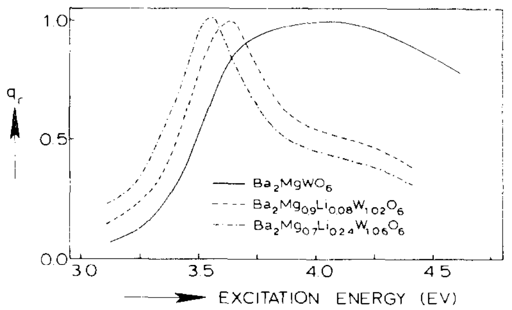

FIG. 2. Excitation spectra of the 2.50-eV emission in the system $Ba_2Mg_{1-x}Li_{0.8x}W_{1+0.2x}O_6$ at 295°K. q_r gives the relative quantum output in arbitrary units.

The luminescence in the system $Sr_{1+x}La_{1+x}Li_{1-0.2x}W_{1+0.2x}O_6$ is rather easy to explain. In $SrLaLiWO_6$, the luminescence is due to isolated, regular tungstate groups. This is confirmed by the fact that in the diluted perovskite $SrLaLiTe_{0.95}W_{0.05}O_6$ the luminescence properties are the same as in $SrLaLiWO_6$ (*10*). For $x > 0$ clusters of tungstate groups occur with absorption at longer wavelength. Excitation into this absorption bands does not yield luminescence. The thermal quenching temperature of the emission of $SrLaLiWO_6$ is about 200°K (*9*). In view of a relation between the quenching temperature and the position of the tungstate absorption band (*11*), it is not surprising that the clusters do not show luminescence. The decrease of the efficiency of isolated tungstate luminescence with increasing value of x can be explained by the combined effect of: (a) a decrease of the concentration of these centers with increasing value of x; and (b) energy transfer from the isolated tungstate groups to the clusters. There is considerable energy overlap between the emission of the isolated tungstate octahedron and the absorption of the clusters.

Clustering of tungstate groups in this system yields, therefore, identifiable killer centers for the luminescence.

Less easy to explain are the results for the system $Ba_2Mg_{1-x}Li_{0.8x}W_{1+0.2x}O_6$. The limiting composition Ba_2MgWO_6 already shows a complicated luminescent behavior with a blue and a yellow emission, of which the former shows concentration quenching in the system $Ba_2MgTe_{1-x}W_xO_6$ (*12*). The present results suggest the presence of three types of centers, viz., the isolated tungstate group (blue emission), tungstate groups with a relatively low number of tungsten neighbors (yellow emission) and tungstate groups with a higher number of tungsten neighbors (no luminescence). This suggestion is compatible with the present and earlier observations and with the results for the previous system, if one realizes that the quenching temperature of the isolated tungstate group in Ba_2MgTeO_6 lies far above room temperature (*12*). This means that small clusters may still show luminescence, as observed before in $Ba_5Li_2W_3O_{15}$ (with a structure in which double layers of WO_6 octahedra occur and a yellow-green luminescence peaking at about 2.5 eV (*13*)) and $BaNa_{0.4}W_{0.6}O_3$ (with cubic perovskite structure and yellow luminescence (*2*)).

If x in the system $Ba_2Mg_{1-x}Li_{0.8x}W_{1+0.2x}O_6$ increases, the concentration of the clusters increases. The blue luminescence especially will be quenched by energy transfer to the nonluminescing clusters. The yellow-emitting center will remain active until the concentration of large clusters is so high that transfer to these centers occurs. The long-wavelength excitation band in Fig. 2 corresponds to the absorption band of the yellow center.

In conclusion, we have shown that deviation from 1:1 order in tungstate perovskites A_2BWO_6 induces the presence of corner-sharing tungstate octahedra which show vibrational and electronic spectra different from those of isolated tungstate octahedra and which modify, and even kill, the luminescence of the A_2BWO_6 compositions.

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